Carbon Dioxide Adsorption on Solvothermolyzed Nano-Dolomite.

by

Ahmad Ashraff bin Ahmad (8167)

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

June 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Carbon Dioxide Adsorption on Solvothermolyzed Nano-Dolomite.

by

Ahmad Ashraff bin Ahmad

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Ye Lwin)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

June 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMAD ASHRAFF BIN AHMAD

ABSTRACT

In this work activated dolomite adsorption was investigated for removal of acidic gaseous pollutants which in this case is Carbon Dioxide. Charring was found to be an effective method for the activation of dolomite based on the literature review and some previous research conducted by chemist. This thermal processing resulted in partial decomposition, yielding a calcite and magnesium oxide structure. Adsorbents were produced over a range of char temperatures (500, 700 and 900 ◦C) and char times (1–8 h). The surface properties and the adsorption capability of rawand thermally treated dolomite sorbents were investigated using SEM, XRD and BET. The sorbate individually investigated was CO2.Using the TPDRO the activated dolomite was tested to produce result as a potentially cost effective material for acidic gases adsorption.

From the results obtained, the results were not like what had been expected. The method used was found not preferable for the project. To continue this research it is recommended to use other options or methods for adsorption experiment.

ACKNOWLEDGEMENT

This research project would not have been possible without the support of many people. The author wishes to express his gratitude first of all to his supervisor, Dr. Ye Lwin who was abundantly helpful and offered invaluable assistance, support and guidance. Deepest gratitude is also due to the coordinator, Dr. Khalik Mohamad Sabil without his help in guidance and assistance this study would not have been successful.

Special thanks also to all his graduate friends, especially from his course mates for sharing the literature and invaluable assistance. Not to be forgotten the technicians from chemical and mechanical department whose helping much in completing the project.

The author would also like to convey thanks to the Ministry and Faculty for providing the financial means and laboratory facilities.

The author wishes to express his love and gratitude to his beloved families; for their understanding and endless love, through the duration of his studies.

TABLE OF CONTENTS

List of Tables

List of Figures

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Every day, the average person inhales about 20,000 liters of air. Every time we breathe, we risk inhaling dangerous chemicals that have found their way into the air. Air pollution includes all contaminants found in the atmosphere. These dangerous substances can be either in the form of gases or particles. Air pollution can be found both outdoors and indoors.

Pollutants can be trapped inside buildings, causing indoor pollution that lasts for a long time. The sources of air pollution are both natural and human-based. As one might expect, humans have been producing increasing amounts of pollution as time has progressed, and they now account for the majority of pollutants released into the air.

In this project, focusing on more to carbon dioxide one of the dangerous pollutant produced by industries nowadays. By using solvothermolyzed, one of the treatment processes, I am hoping that this project will come out with a great results and can be useful for the research that being done nowadays and the next generations.

1.2 Problem Statement

Carbon dioxide (CO_2) is one of the major pollutants in the atmosphere. Major sources of CO_2 are fossil fuels burning and deforestation. "The concentrations of CO_2 in the air around 1860 before the effects of industrialization were felt, is assumed to have been about 290 parts per million (ppm). In the hundred years and more since then, the concentration has increased by about 30 to 35 ppm that is by 10 percent". (Breuer 67) Industrial countries account for 65% of CO_2 emissions with the United States and Soviet Union responsible for 50%. Less developed countries (LDCs), with 80% of the world's people, are responsible for 35% of CO_2 emissions but may contribute 50% by 2020. "Carbon dioxide emissions are increasing by 4% a year". (Miller 450)

In 1975, 18 thousand million tons of carbon dioxide (equivalent to 5 thousand million frtons of carbon) was released into the atmosphere, but the atmosphere showed an increase of only 8 billion tons (equivalent to 2.2 billion tons of carbon". (Breuer 70) The ocean waters contain about sixty times more CO_2 than the atmosphere. If the equilibrium is disturbed by externally increasing the concentration of CO_2 in the air, then the oceans would absorb more and more CO_2. If the oceans can no longer keep pace, then more CO_2 will remain into the atmosphere. As water warms, its ability to absorb CO_2 is reduced.

CO_2 is a good transmitter of sunlight, but partially restricts infrared radiation going back from the earth into space. This produces the so-called greenhouse effect that prevents a drastic cooling of the Earth during the night. Increasing the amount of CO_2 in the atmosphere reinforces this effect and is expected to result in a warming of the Earth's surface. Currently carbon dioxide is responsible for 57% of the global warming trend. Nitrogen oxides contribute most of the atmospheric contaminants.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objectives of this experiment are:

1. To study the effectiveness of carbon dioxide adsorption using solvothermolyzed dolomite
2. To find the best condition by considering the composition, type of solvent and method of preparation in order to obtain the maximum carbon dioxide adsorption rate and capacity.

1.3.2 Scope of Study

The dolomite will be experimented at nano size. The temperature will be set at 110°C, 500°C, 700°C, and 900°C during heating phase. There is no pressure manipulation for this experiment, so it will be at normal pressure. In this experiment, a machine called as ultra-sonic cleaner will be used to generate the wave which will treat the dolomites. The dolomites will be put inside three different kind of solvent. This is what we understand with solvothermolyzed. In this project, the solvent that will be used are water, ethanol and tert-butanol.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 Dolomite

The generic term "limestone" embraces mineral deposits that are comprised of the carbonates of calcium and magnesium, but it is important to distinguish among magnesian limestone, dolomitic limestone, and dolomite. Van Tuyl(52) and Clarke (7,8) reviewed the geochemical theories for the formation of dolomite. Clarke (7) observed that "the term 'dolomite' is sometimes used by geologists as equivalent to magnesian limestone. Properly, the word should be restricted to the definite double carbonate," and Knibbs (16) concluded likewise.

The Association of Official Agricultural Chemists defines dolomite as "a mineral composed chiefly of carbonates of calcium and magnesium in substantially unimolal proportion." Dolomite is rhombohedral and identifiable through its resistance to dilute solutions of acids and by the logwood test . Knibbs noted that "there has been much speculation and research on the nature of dolomite" and concluded that "dolomite may conceivably be a mixture, a solid solution, or a compound" (16, p. 81). According to Azbe (3, p. 37), "the two carbonates do not appear to be in either a physical mixture or in a chemical combination," but MacIntire and Shaa (32) proved that true dolomite is the double carbonate, as is also the dolomite fraction of a dolomitic limestone, and substantiated the findings reported by Leather and Sen (18).

2.2 XRD of Dolomite

In situ X-ray diffraction (XRD) was used to elucidate the thermal decomposition of dolomite. As opposed to previous efforts that required samples be heated to a specific temperature and held for the duration of an X-ray scan, data was collected at 4°C intervals while continuously heating the sample at 3°C/min. Under CO_2, dolomite decomposed directly to $CaCO_3$, accompanied by the formation of MgO between 550 and 765°C.

No evidence was offered for the formation of either CaO or $MgCO_3$ during this first stage. Calcite decomposed to CaO between 900 and 960°C, under air, simultaneous formation of $CaCO_3$, CaO and MgO accompanied dolomite decomposition between 700 and 740-750°C. At

the latter temperature, the calcite began to decompose even though a significant amount of dolomite was still present. Simultaneous decomposition of the two carbonates terminated at 780°C. (Philip Engler, Mark W. Santana, Martin L. Mittleman and David Balazs, 1988)

2.3 Calcination of Dolomite

The dolomite modified with acetic acid solution was proposed as a CO_2 sorbent for calcination carbonation cycles. The carbonation temperature in the range of 630 °C–700 °C is beneficial to the carbonation reaction of modified dolomite. The carbonation conversion for modified dolomite is significantly higher than that for original sorbent at the same reaction conditions with increasing numbers of reaction cycles. At the high calcinations temperature over 920 °C modified dolomite can maintain much higher conversion than unmodified sorbent. The mean grain size of CaO derived from modified dolomite is smaller than that from original sorbent with increasing numbers of reaction cycles.

The calcined modified dolomite possesses greater surface area and pore volume than calcined original sorbent during the multiple cycles. The pore volume and pore area distributions for calcined modified dolomite are also superior to those for calcined unmodified sorbent during the looping cycle. The modified dolomite is proved as a new and promising type of regenerable CO2 sorbent for industrial applications.(Ying-jie Lia, Chang-sui Zhao, Lun-bo Duana, Cai Lianga, Qing-zhao Lia, Wu Zhoua and Hui-chao Chen, 2008)

2.6 Surface Area Determination using BET

Several methods and theoretical models which are used to measure the surface area have been developed Because of its ease of use, its definitiveness and its straightforward applicability, the B.E.T. (Brunauer, Emmett and Teller) theory (S. Brunauer, P.H. Emmett and E. Teller, J. Amer. Chem. Soc. 60, 309, (1938)) is almost universally employed in surface area measurement. The principle of the Quantasorb surface area analyzer is based on the B.E.T. theory, which is a commonly used method of determining the specific surface of solids by the physical adsorption of a gas on the surface of a solid. The determination of the monolayer capacity [V.sub.m], which is defined as the quantity of adsorbate required to cover the adsorbent with a monolayer, leads to the determination of specific surface areas in the B.E.T. method. Usually a second layer may be

forming before the monolayer is complete, but [V.sub.m] is determined from the isotherm equations irrespective of the influence of multilayers. The background knowledge about B.E.T. theory and the principle using the B.E.T. Surface area analyzer to measure surface areas is well discussed by T. Allen (T. Allen, "Particle size measurement," 2nd ed. John WIley & Sons, New York, 1975), S. Lowell and Joan E. Shield (S. Lowell, Joan E. Shield, "Powder surface area and porosity" 2nd ed. Chapman and Hall, London, 1984)

2.5 Carbon Dioxide Adsorption

The adsorption of water vapor and carbon dioxide at room temperature in relation to carboxylic functional groups on the surfaces of 20 different types of coal was examined. The carboxylic functional groups on the surface of coal may be considered the preferential sites of adsorption when compared with the other groups. The adsorption of water vapor and carbon dioxide was found to increase in proportion to the square root of the carboxyl group concentration, regardless of the partial pressure or the gas species. Assuming functional group adsorption sites to be present on the surfaces of hydrophobic matrices and adsorption to occur in a liquid-like closed packed state, the adsorption on coal was determined based on the carboxyl group concentration on the coal surface, the molecular cross section and the molecular weight of the adsorbate. The surface area did not depend on the type of adsorbate, as was observed for water vapor and carbon dioxide adsorption on coal. (J. Nishino, 2000)

CHAPTER 3
PROJECT METHODOLOGY

3.1 Dolomite

This experiment needs a nano size of dolomite. Instead of using the normal solid rock of dolomite which needs to grind in order to obtain nano size, I bought the dolomite that already packed in powder. This will save a lot of time and budget.

3.2 Preparation of the Solvent

In this project, alcohol and water will be used as the solvent. Ethanol and tert- butanol (2-Methylpropan-2-ol) are chosen after consideration of their properties such as boiling point, solubility, molar mass and others. Also, these solvent are chose due to availability in chemical lab's storage. This will save the time and probability of error during the preparation of the solvent. If want to prepare the solvent myself from raw, it will consume a lot of time and a little mistake in preparing the solvent will gives a big impact to my project.

The dolomite particles will be put inside a small air-sealed vessel with the solvent. This mixture will be treated using ultrasound cleaner at a high temperature at a range of times.

3.3 Samples Treatment

First of all, the dolomite particles need to be treated using ultra sound. Ultra sound is chose as a way of heating instead of using normal heating in order to experiment the effectiveness of dolomite to adsorb acidic gas by using this treatment. Ultrasonic cleaner which can produce both heating power and ultrasound (wave) will be used in this project. The samples will be going trough the treatment process for at least 8 hours. The setting of the treatment list out below

Properties	
Temperature	70°C
Ultrasound Power	100 Hertz

Table 1 - Ultra Sonic Condition Setting

Any modifications might occur during the experiment.

3.4 Scanning Electron Microscope (SEM)

SEM will be used to see the surface of:

1. Raw Particles
2. 3 samples treated with different solvent
    - Dolomite + Water
    - Dolomite + Ethanol
    - Dolomite + tert-butanol

    (All will be scanned after being dried at temperature of 110°C)
3. 3 samples heated at 3 different temperature 500°C, 700°C, 900°C

The results will be compared and discussed. Any modifications might occur during the experiment.

3.5 X-ray diffraction (XRD)

In XRD, the sample will be scanned to get the composition graph in order to ensure the samples already went through calcinations process. The samples involved same as the samples scanned using SEM, which are:

1. Raw Particles
2. 3 samples treated with different solvent
    - Dolomite + Water
    - Dolomite + Ethanol
    - Dolomite + tert-butanol

    (All will be scanned after being dried at temperature of 110°C)
3. 3 samples heated at 3 different temperature 500°C, 700°C, 900°C

The results will be compared and discussed. Any modifications might occur during the experiment.

3.6 Determination of the surface area

All of the samples will be analyzed for specific surface area using BET. BET theory is a rule for the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

3.7 Carbon Dioxide Adsorption

The last phase of my experiment is injecting carbon dioxide to the particles in order to analyze the effectiveness of dolomite to adsorb carbon dioxide. There are several choices of equipment for me to undergo this process. The equipment suggested such as

1. Carbon Dioxide Adsorption Column
2. Thermal gravimetric analysis (TGA)
3. Temperature Programmed Desorption; Desorption; Reduction & Oxidation (TPDRO)

For the first choice, CO_2 Adsorption Column, the equipment cannot accept powder samples because it will affect the pipeline and it will cost a lot to repair if the incident occurs. TGA is currently under maintenance and the last choice left is using TPDRO. This machine can operate for various usages like below:

* Thermal Programmed Desorption
* Thermal Programmed Reduction
* Thermal Programmed Oxidation
* Pulse Chemisorptions
* Catalysts Activation

Any modifications might occur during the experiment.

CHAPTER 4
PROJECT WORK

4.1 Samples preparation

4.1.1 Procedures

1. Dolomite samples weighted approximately 10g. The samples prepared for three different solvent which are water, ethanol and tert-butanol.
2. The samples inserted into each conical flask and labeled properly.
3. The flask then will be put inside the ultra sonic cleaner that already filled with water (water bath).
4. The equipment switched on after the setting already adjusted.
5. Leave the process and take out the samples after 8 hours.

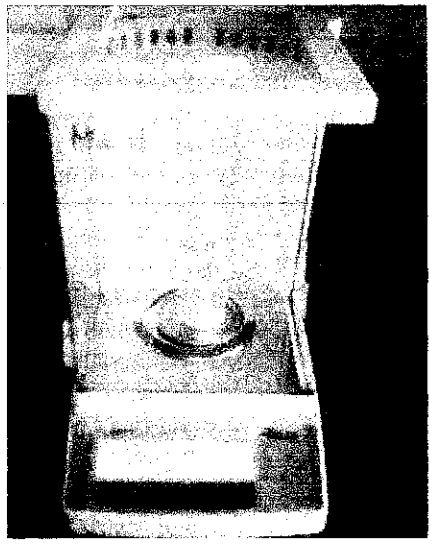

Figure 1 -Electric Scale used for measuring weight

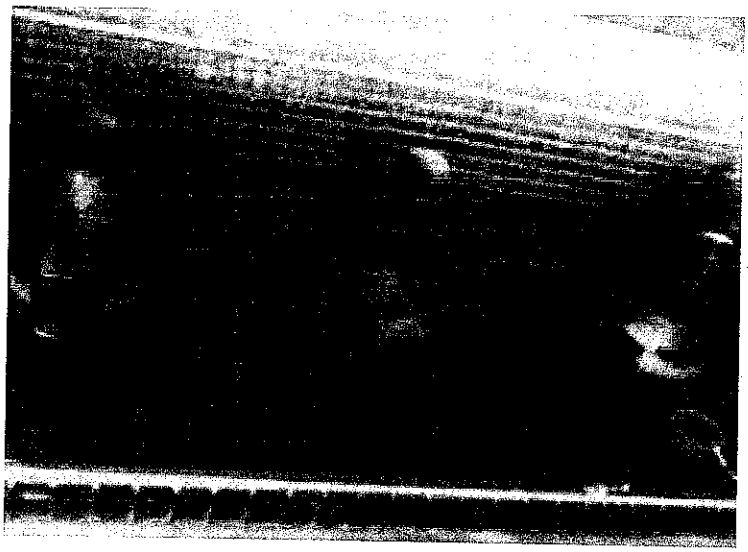

Figure 2 - Samples during treatment process

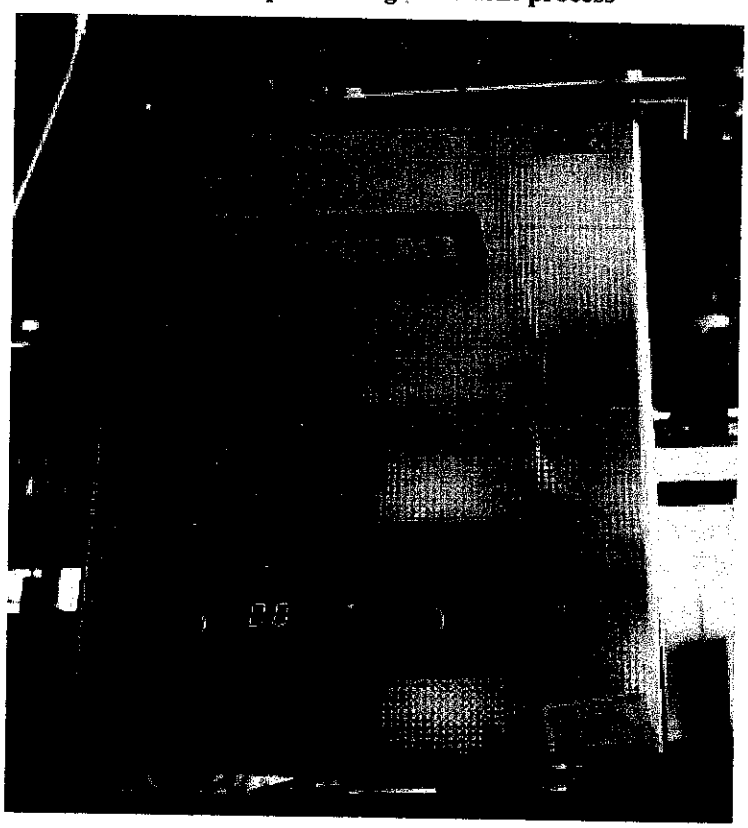

Figure 3 - Ultra Sonic Cleaner

4.1.2 Summary

The experiment had done by me starting last semester holiday. During the preparation and treatment of the samples using ultrasound cleaner, there were some modifications had been made due to equipment problem. Using the ultra sonic cleaner, the treatment process initially can be operated well where the wave produced can be adjusted according to the methodology stated before. But the equipment itself had some problems where it cannot be adjusted to operate for 8 hours automatically. So, the process of timing had been done manually.

Besides, there were other problems occur regarding this equipment such as the equipment itself always shutdown itself and no flask clipper provided with this equipment. This will produce non persistent results. Some modifications had done during this phase.

1. The setting being checked every one hour during the treatment
2. The flask clipper attached by using tape to the cage provided.

The samples had successfully treated after a few tries.

4.2 Heating/Drying

4.2.1 Procedures

1. The samples that already gone trough treatment process was heated at 110°C for a day. This is for drying purpose.

2. Next, the samples will be heated at three different high temperatures which are 500°C, 700°C and 900°C. Let the samples for 3 hours after the temperature is constant. Here, calcinations process will occur.

3. After the process, all of the samples need to be scanned using XRD and SEM. Then it will be analyzed and discussed.

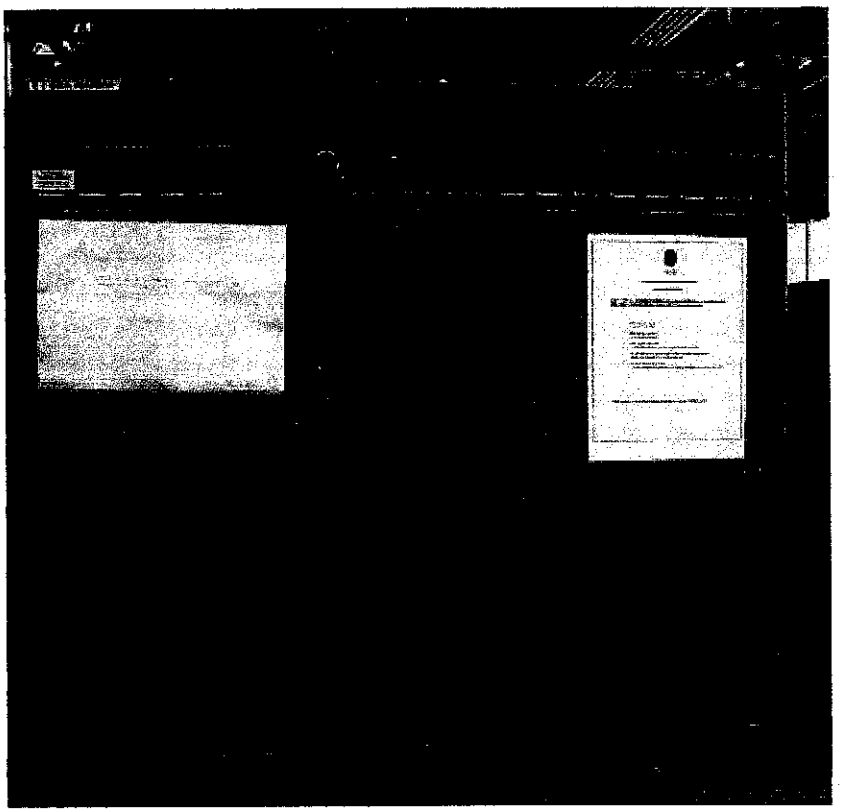

Figure 4 - Oven used for drying

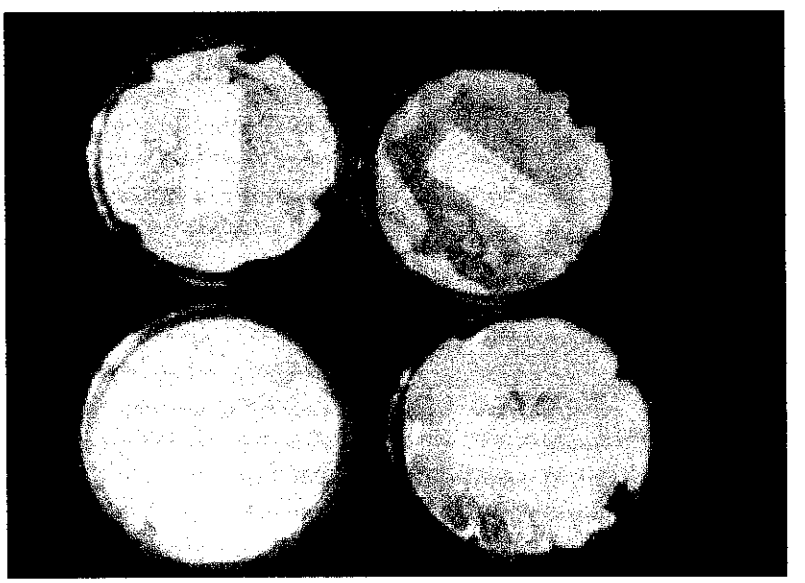

Figure 5 - Samples after dried

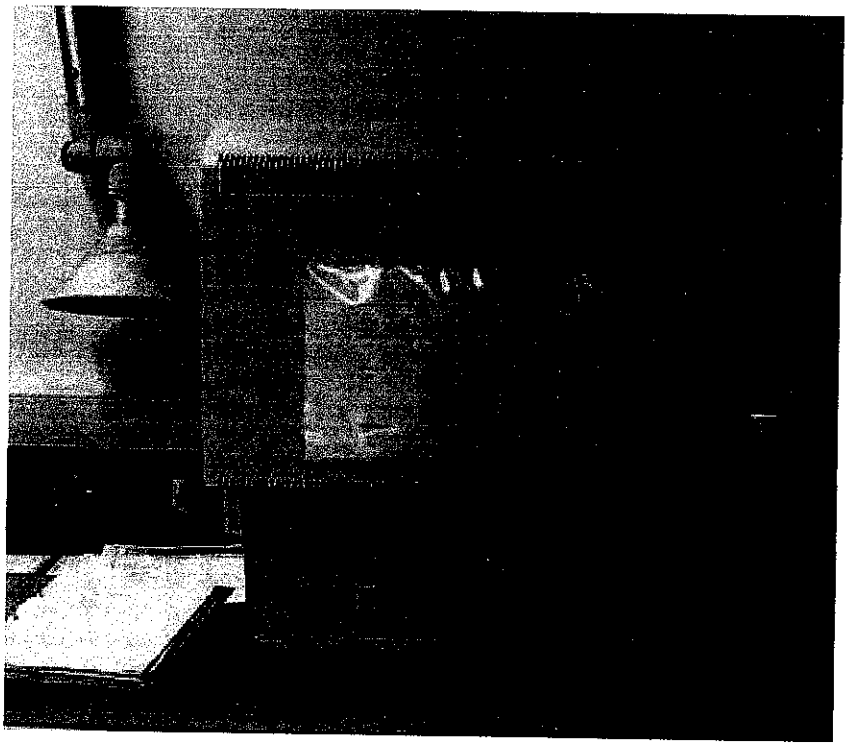

Figure 6 - Furnace used for heating process

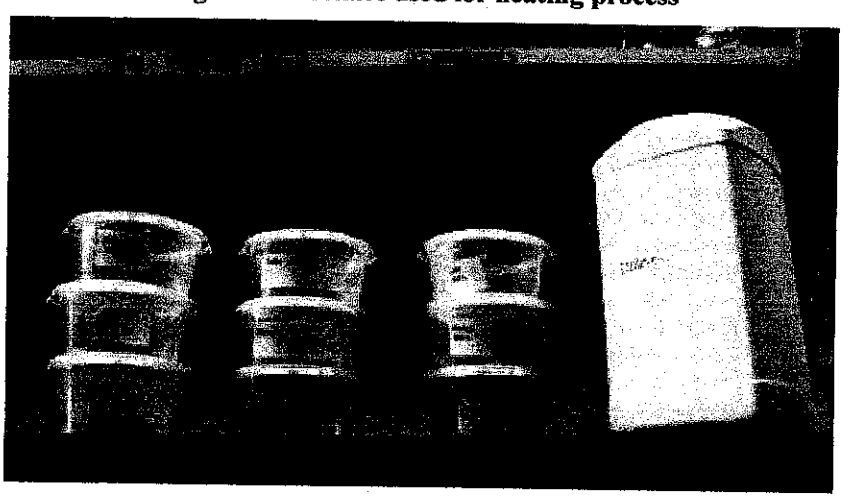

Figure 7 - Treated samples

4.2.2 Summary

After the preparation phase, the samples next must going trough heating process at high temperature. The purpose of this process is to compare the different adsorption ability of carbon dioxide on dolomite based on variable temperature. It has been decided to use three different temperatures which are 500°C, 700°C and 900°C. Firstly at 110°C, the samples heated using

oven and let it in drying process for at least a day. The furnace was used to heat up the samples at the higher temperature ensure that the samples undergo the calcinations process. Using furnace, the samples must heated at the decided temperature constantly for 3 hours minimum.

During the heating process using furnace, there was a problem to heat the samples. The furnace cannot reach more than 650°C in 8 hours which is the duration where the laboratory is opened for students. The furnace needs to be shutdown sharp at 5pm in order to prevent any bad incident happen. Because of this problem, I need to cancel out to heat the samples at 700°C and 900°C. After a few discussions with my supervisor, we decided to heat the samples and just let the temperature goes to the maximum it can and leaves it starting 8am until 5pm. So, the final temperature decided to be heated are 500°C and 650°C.

4.3 Analyze using SEM

4.3.1 Procedures

1. The samples will be treated first before put inside the SEM machine.
2. During the treating process, black gold will be sprayed to the surface of the samples so this will give an image during scanning process.
3. The samples will be scanned and the favorable image at the desire magnification will be printed out.

4.3.2 Summary

Samples analyzing conducted by the technician himself. Only 8 samples can undergo for one session of scanning at a time. The samples need to be treated for at least 30 minutes before scanning process. Black gold sprayed at their surface in order to give reflection during scanning where this will give an image of the samples. By looking from the monitor, a favorable surface and depth of scanning printed out.

4.4 Analyze using XRD

4.4.1 Procedures

1. Overall process will be conducted by technician. No student allowed during the working process since the process need x-ray radiation which harmful to people.

4.4.2 Summary

Since the analyzing must be done by the technician himself, there is no specific procedure that can be explained by me.

4.5 Determination of the surface area using BET

4.5.1 Procedures

1. The samples will be undergoing degassing process for treatment purpose. It will be left for at least 3-4 hours.
2. The samples then will be scanned and analyzed using BET.
3. All the procedures will be handled by the technician.

4.6 Carbon Dioxide Adsorption

4.6.1 Carbon Dioxide Adsorption using TPDRO

1. The samples first will be weighted approximately 0.2g to 0.3g
2. It will undergo pre-treatment process using Nitrogen gas flow for at least 10 to 20 minutes.
3. After the pre-treatment, the samples then will undergo TPD process. In this process, Helium gas and pure Carbon Dioxide gas will be flown together since there is no CO_2/N_2 mixture tank available.
4. The result will be analyzed and discussed.

4.6.2 Summary

During this phase, the samples first weighted approximately 0.2g to 0.3g. There is no need to use a large amount of samples during this phase. The samples will be undergoing pre-treatment process using Nitrogen after weighted. The N_2 gas started at 110°C will be sent via pipeline at rate of 20 ccm/min. Then it will be held for 5 minutes. After that, Carbon Dioxide gas will be sent at flow rate of 20 ccm/min at will be stopped when the temperature reached to 500°C. It will be held for at least 15 minutes. The purpose is to ensure there is an adsorption process occurs.

To know the amount of CO_2 gas adsorbed, TPD process will undergo after the pre-treatment. The chosen gas for this purpose is Helium since its thermal conductivity is higher compare to CO_2.

This procedure suggested by the technician himself due to unavailability of CO_2/N_2 mixture tank. To proceed with this procedure, we need to try and error the time held for CO_2 to ensure the samples is given enough time to undergo adsorption process.

CHAPTER 5
RESULT AND DISCUSSION

5.1 Scanning Electron Microscope (SEM)

Below are the images of micro scanning on the surface of sample particles using SEM.

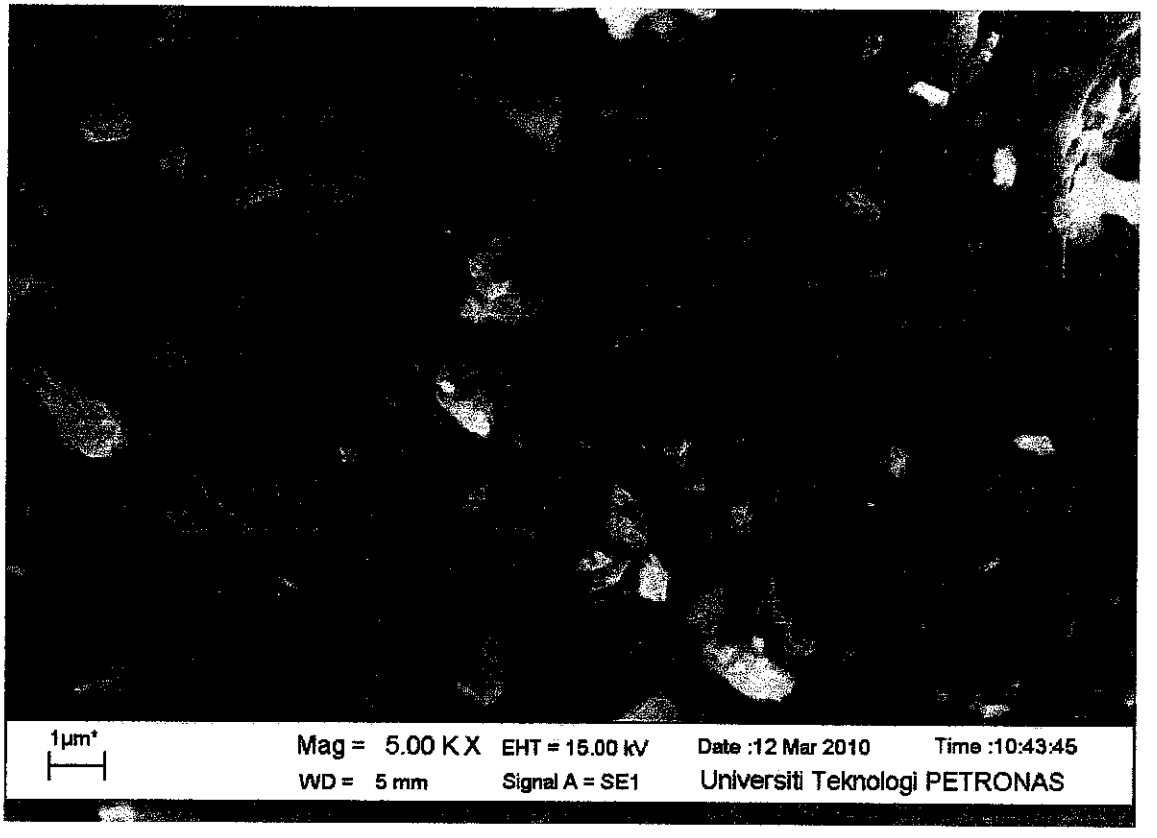

Figure 8 – SEM of surface of raw dolomite

Figure 9 - SEM of surface of dolomite + water at 110°C

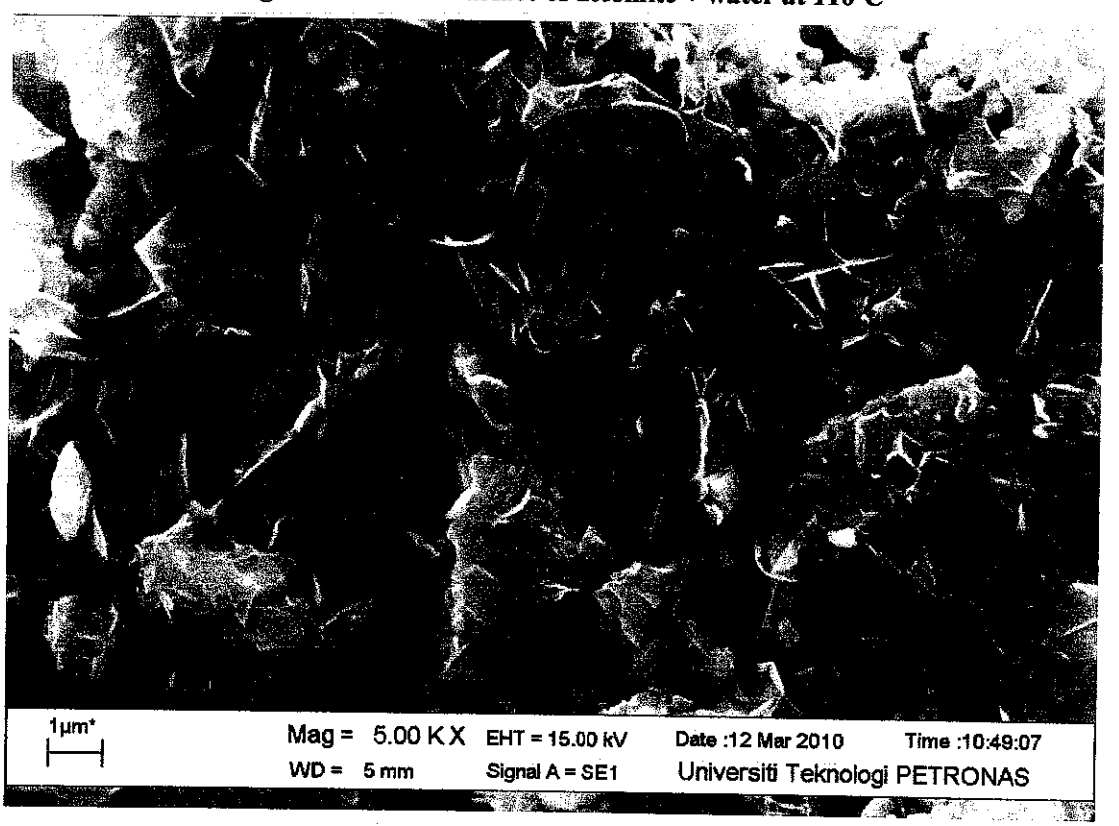

Figure 10 - SEM of surface of dolomite + water at 500°C

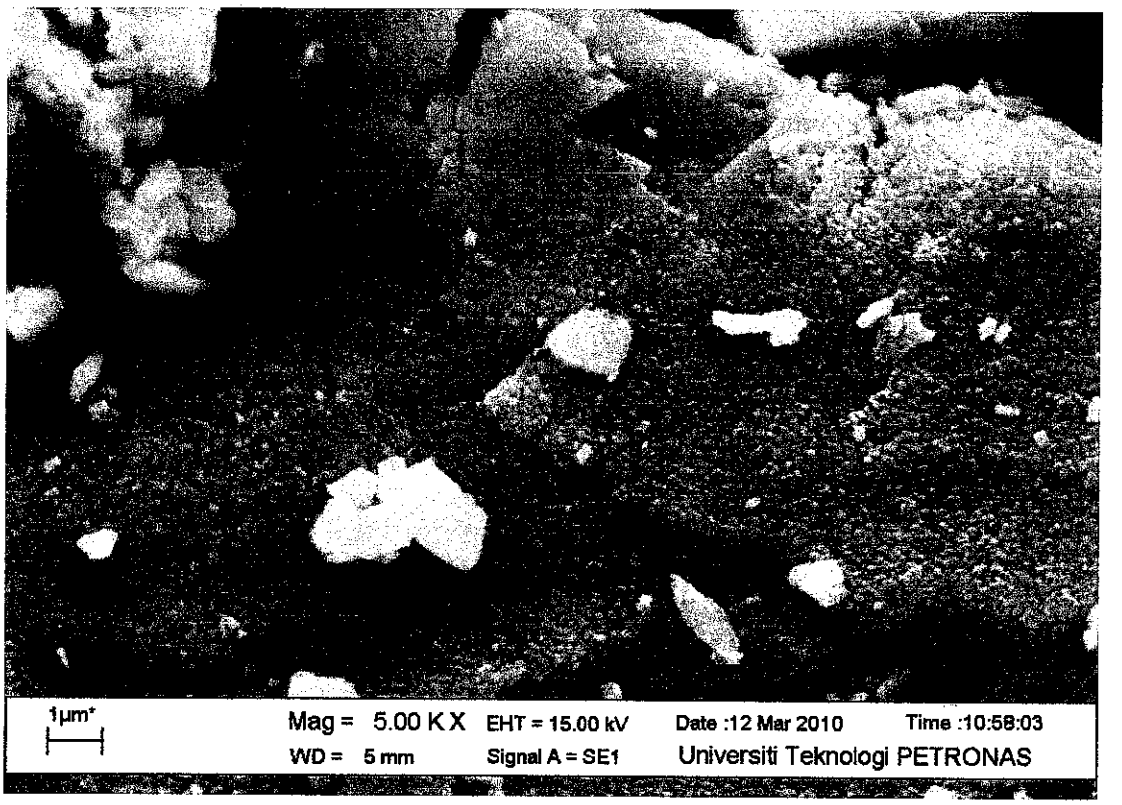

Figure 11 - SEM of surface of dolomite + water at 670°C

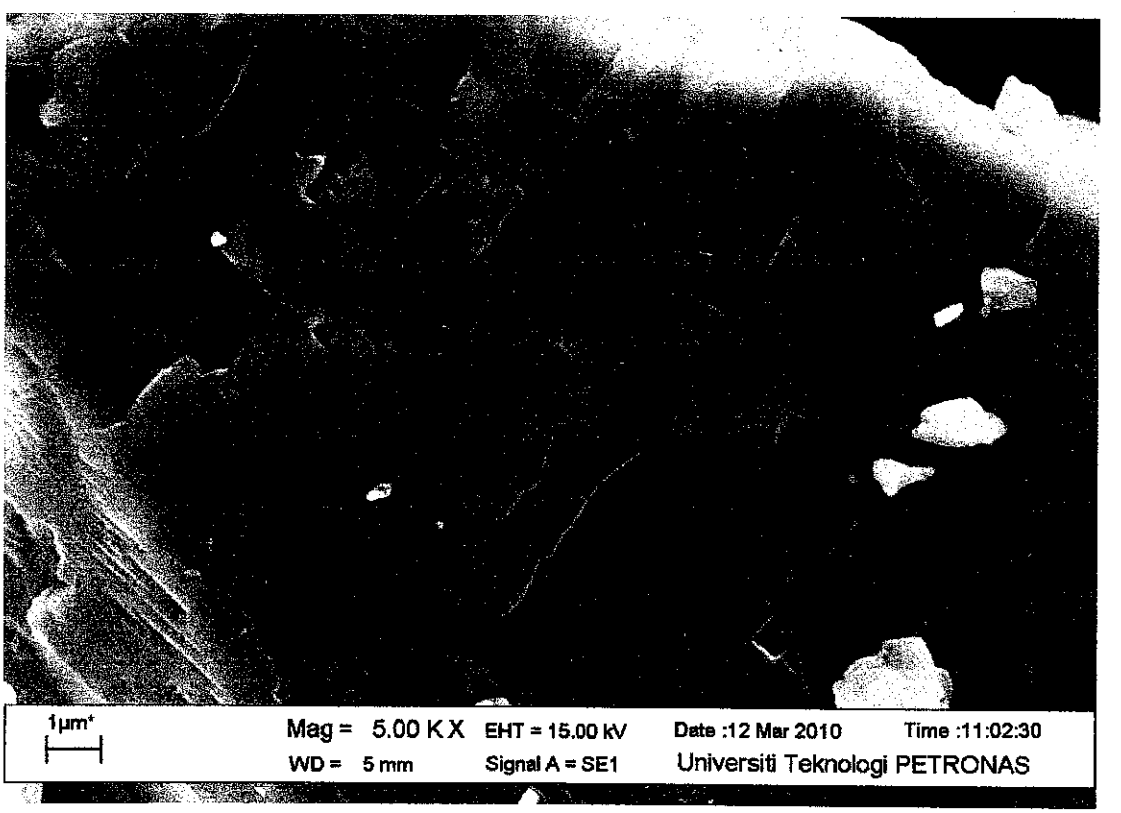

Figure 12 - SEM of surface of dolomite + ethanol at 110°C

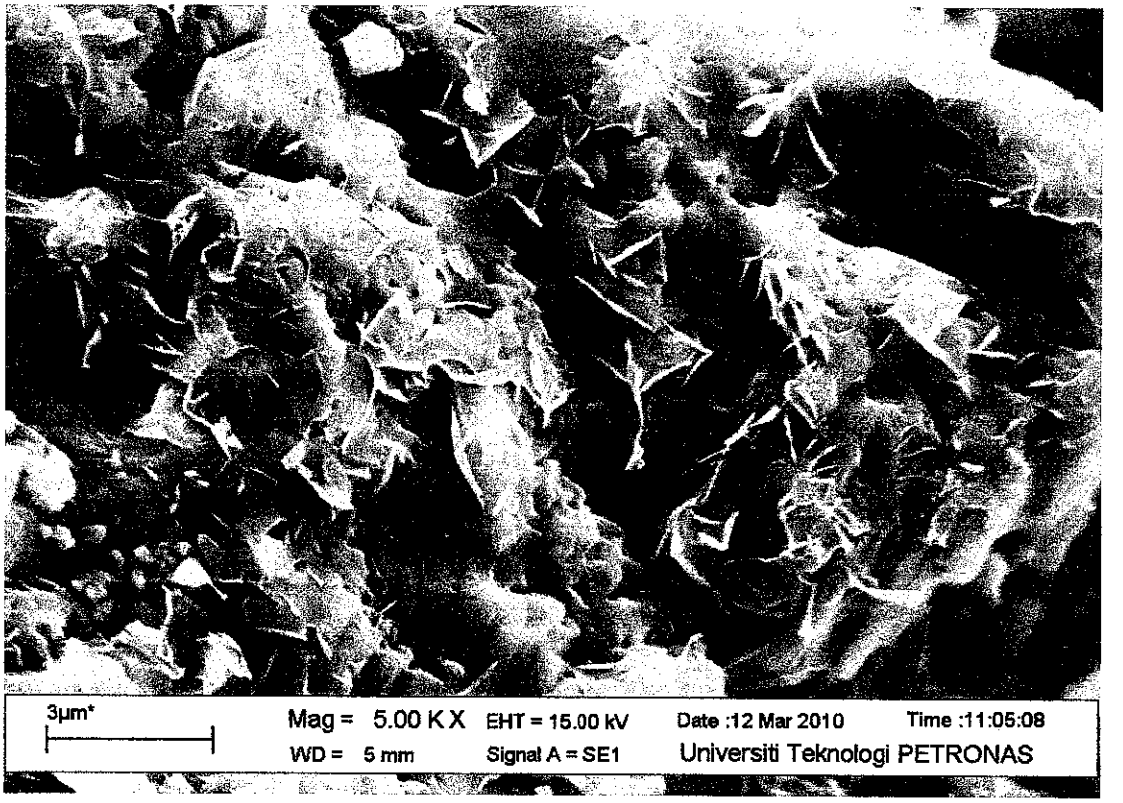

Figure 13 - SEM of surface of dolomite + ethanol at 500°C

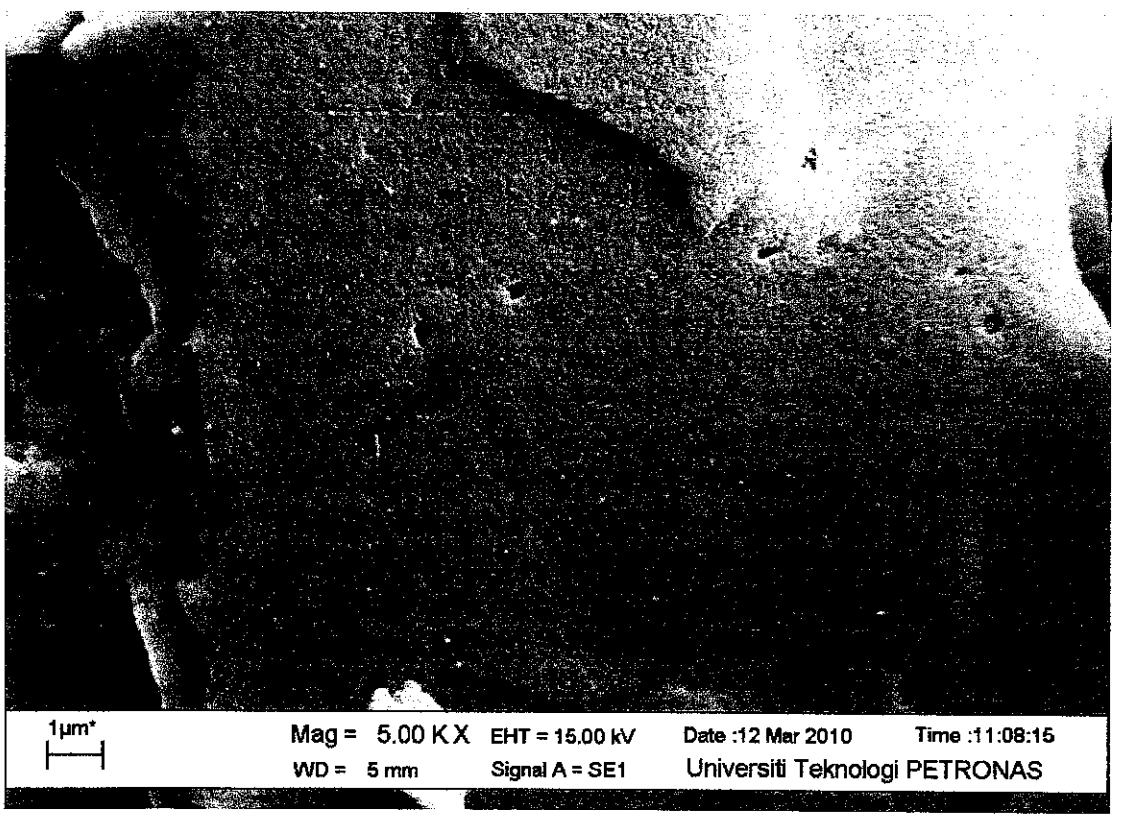

Figure 14 - SEM of surface of dolomite + ethanol at 670°C

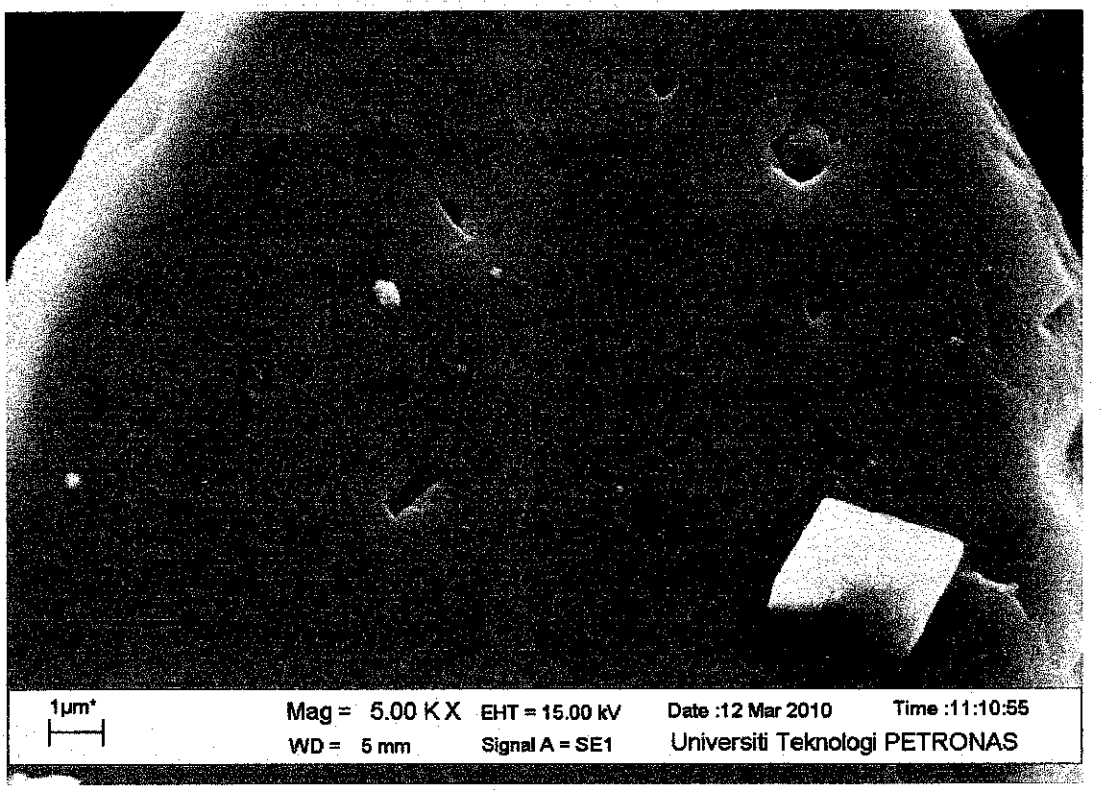

Figure 15 - SEM of surface of dolomite + tert-butanol at 110°C

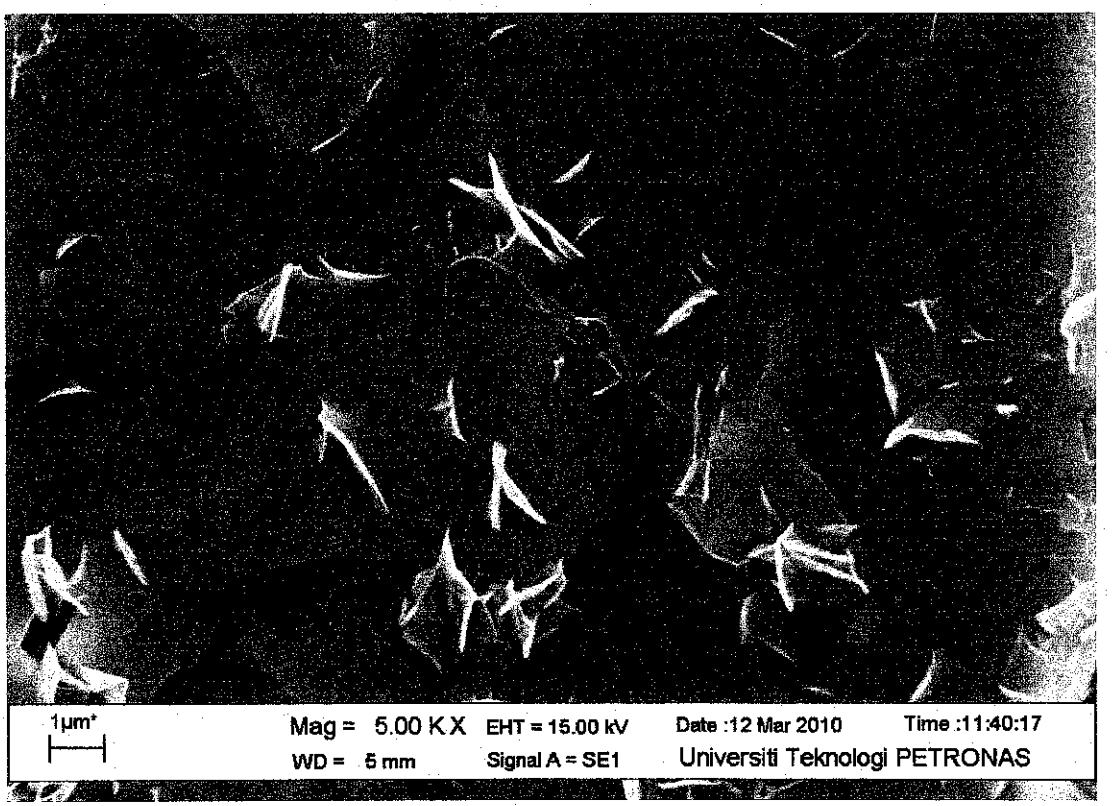

Figure 16 - SEM of surface of dolomite + tert-butanol at 500°C

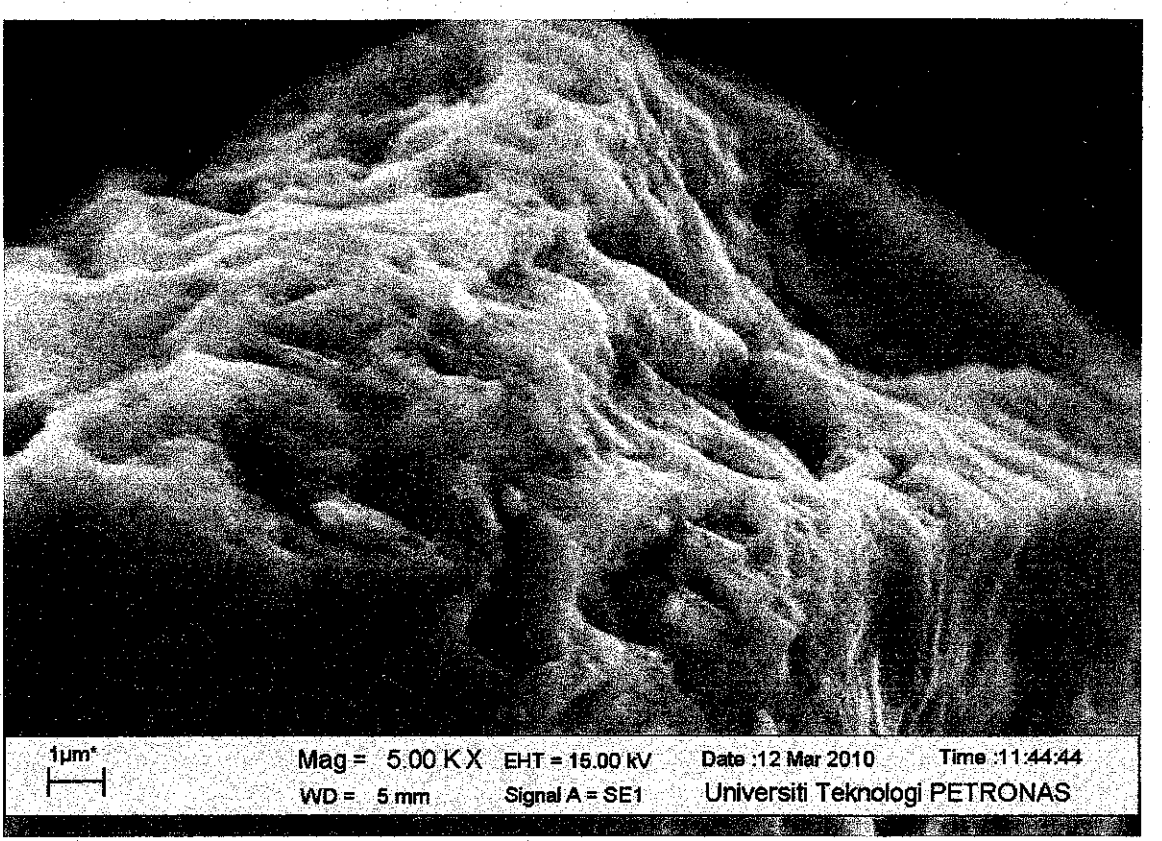

Figure 17 - SEM of surface of dolomite + tert-butanol at 670°C

5.1.1 Basic Principles

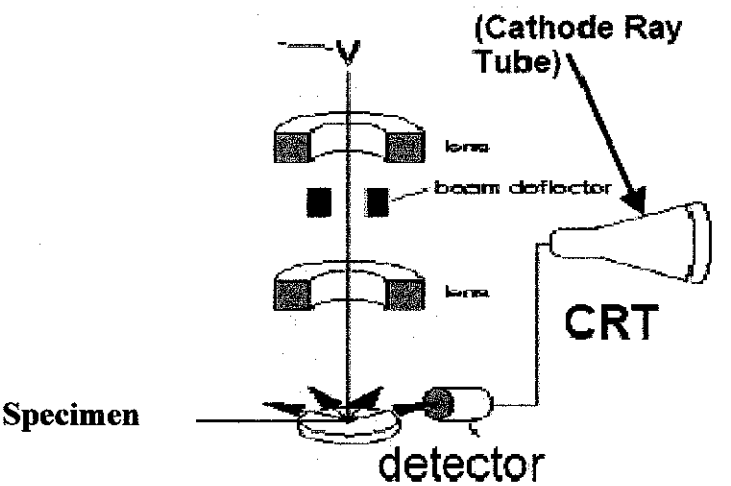

Figure 18 - Principal Features of SEM

Electron microscopes are scientific instruments which using a beam of energetic electrons to examine objects on a very fine scale. SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample. There are 3 main parts of components in SEm which described below:

1. Electron optical column consists of:
    a. Electron source to produce electrons
    b. Magnetic lenses to de-magnify the beam
    c. Magnetic coils to control and modify the beam
    d. Apartures to define the beam, prevent electron spray, etc.
2. Vacuum systems consists of :
    a. Chamber which "holds" vacuum, pumps to produce vacuum
    b. Valves to control vacuum, gauges to monitor vacuum
3. Signal Detection and Display consists of:
    a. Detectors which collect the signal
    b. Electronic which produce an image from the signal

5.1.2 Summary of SEM analyzing process

From the results obtained from SEM, can see there is a change of dolomite surface at different temperature. Looking at the image of raw surface of dolomite can see the surface is flat and smooth without any clear pores.

As the temperature increases, there is a slight change on the surface. Can see for all the samples after dried at 110°C, tend to show some cracked surface. At 500°C, all the samples show a crystalline structure. And finally at 670°C, the maximum temperature that the samples had been heated gives the same image where there is a porous structure with evidence that a meso and macro-pore structure being formed. It is clear from this analysis that charred or calcined dolomited hat the potential to act as an adsorbent, albeit with a relatively low surface area compared to commercial adsorbent.

SEM analysis performed for all samples shows the different structure as the temperature increases. This dissociation is endothermic which means that heat exchanges must take place at the surface and inside the particles.

5.2 X-ray Diffraction (XRD)

The results obtain from x-ray diffraction process in determining the component composition in the samples shown below.

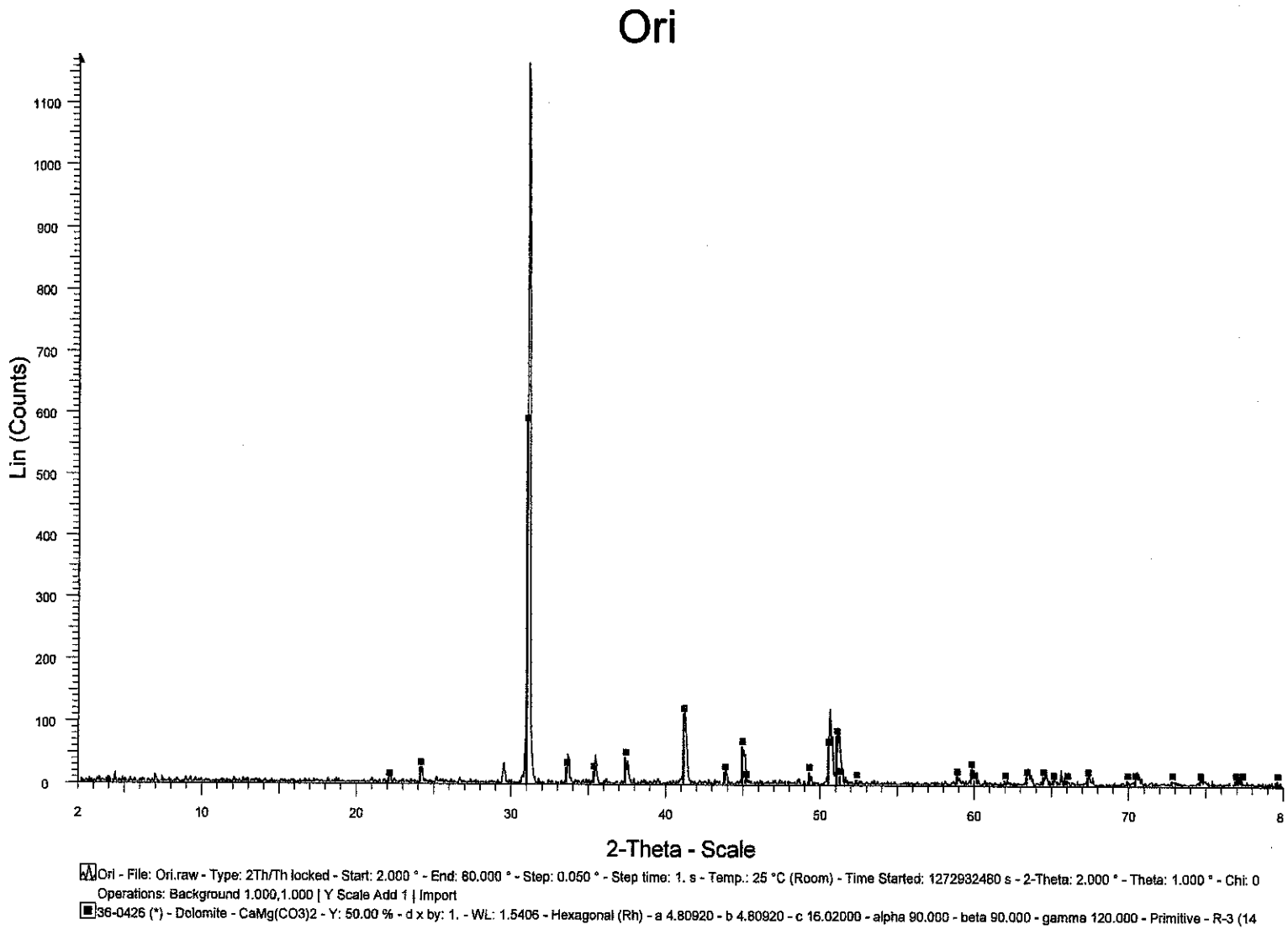

Figure 19 - Raw Dolomite

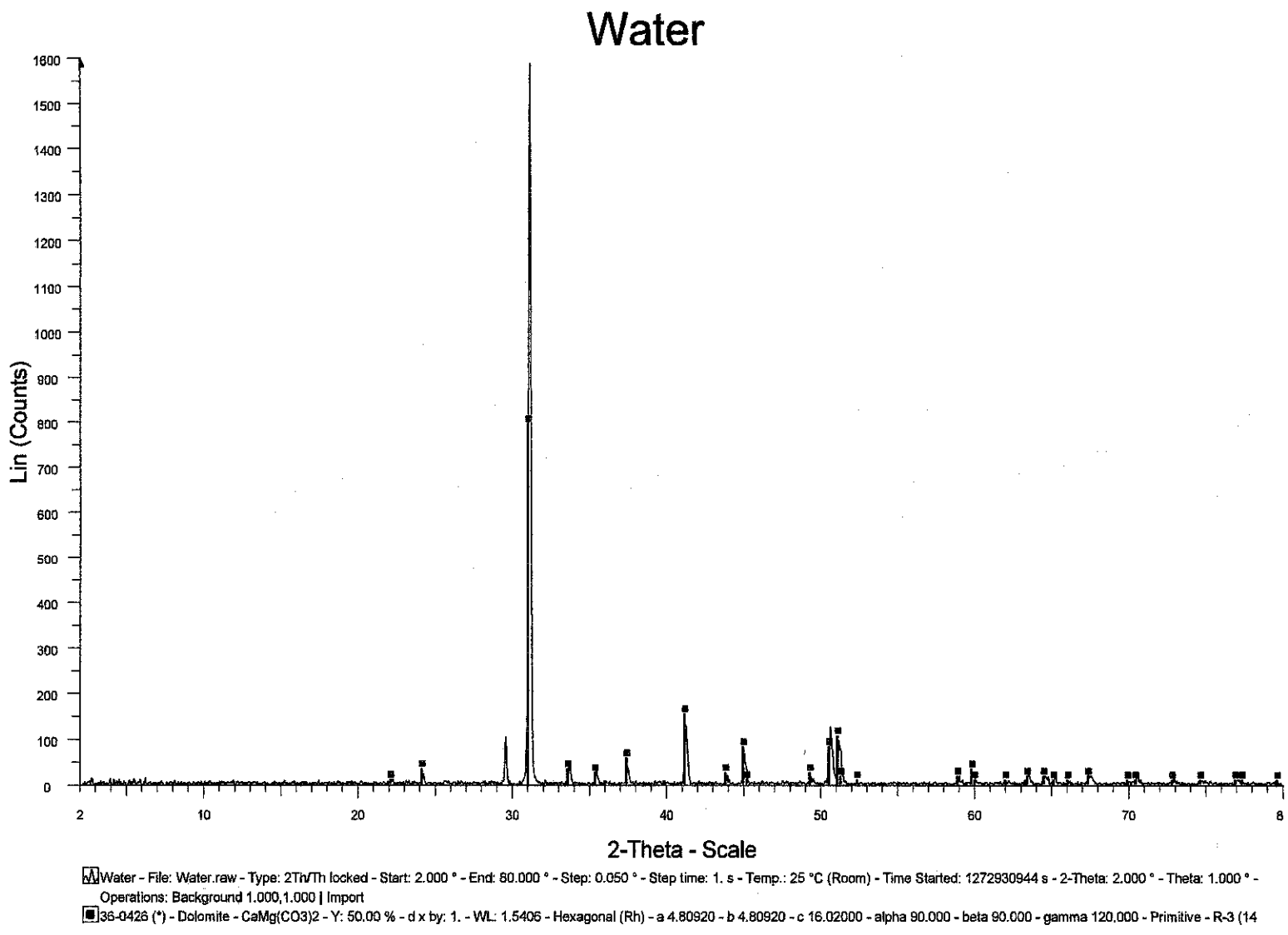

Figure 20 - XRD of dolomite + water at 110°C

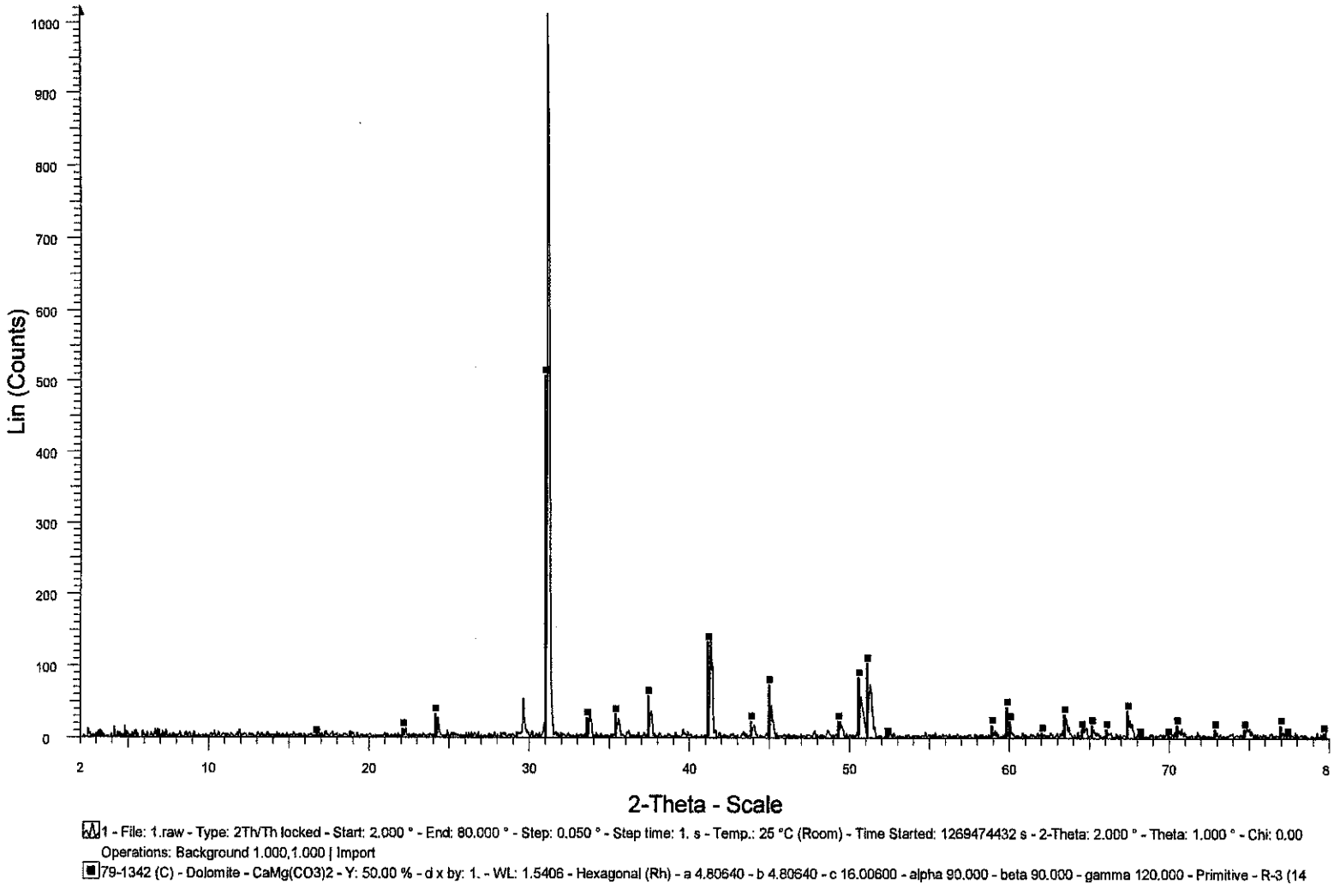

Figure 21 - XRD of dolomite + water at 500°C

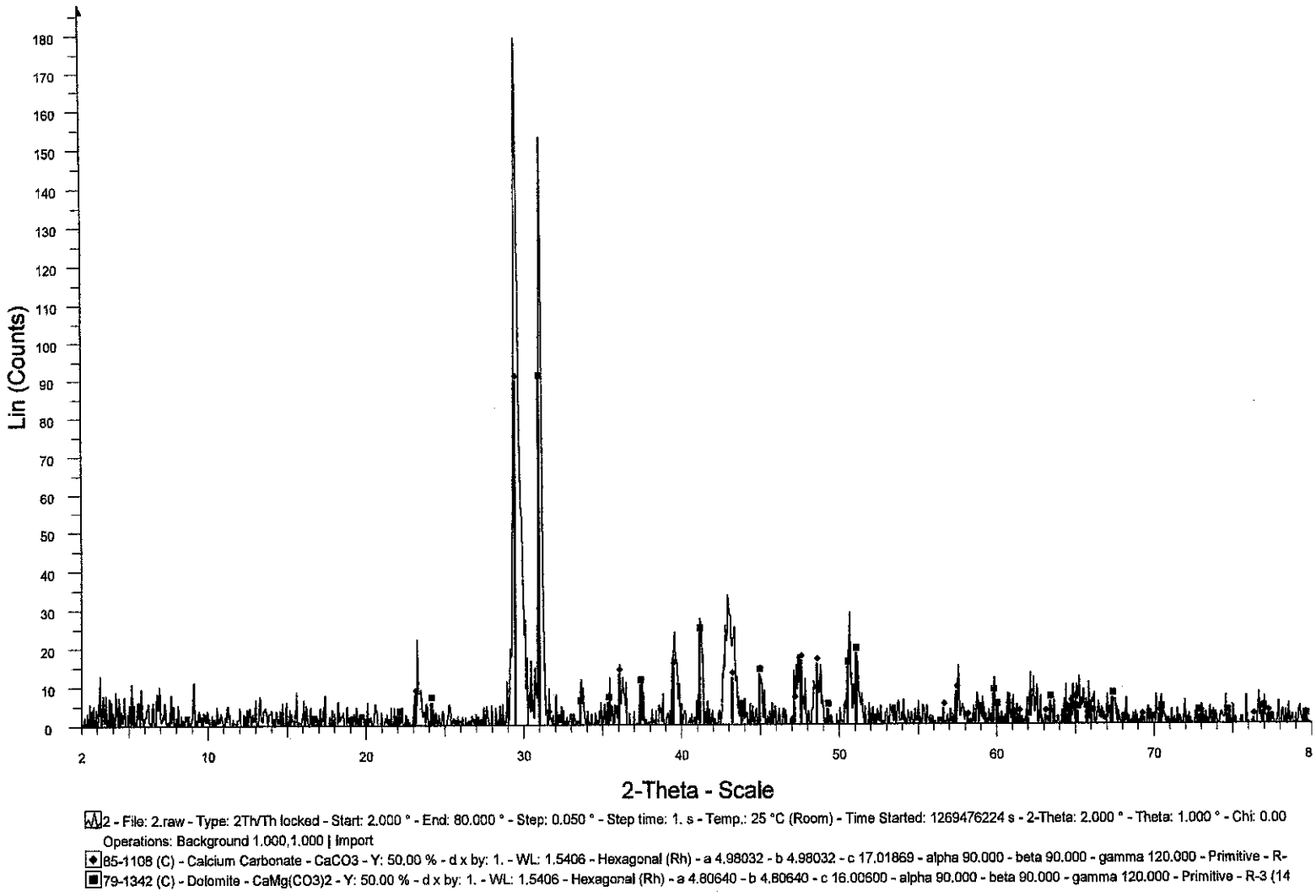

Figure 22 - XRD of dolomite + water at 670°C

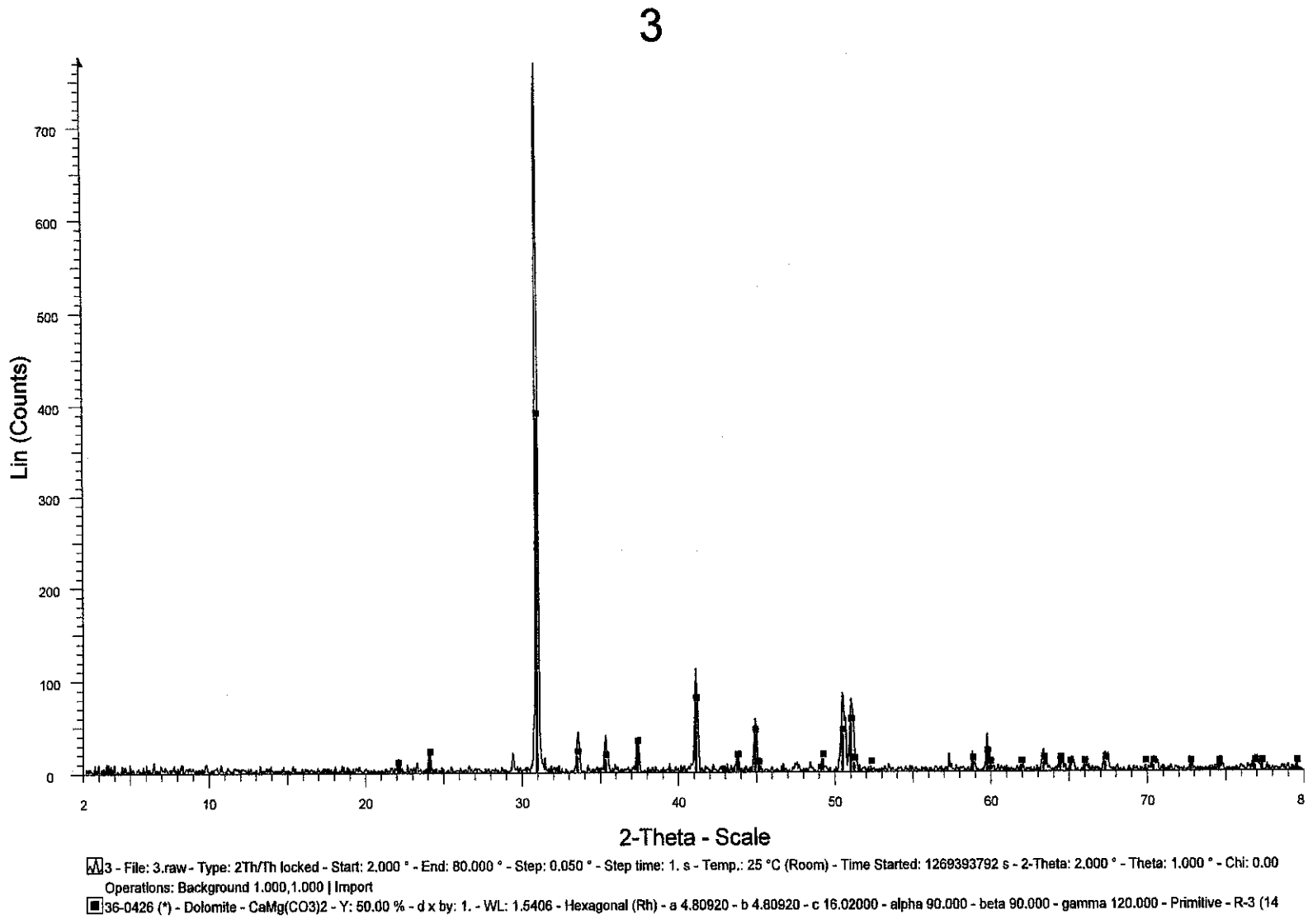

Figure 23 - XRD of dolomite + ethanol at 110°C

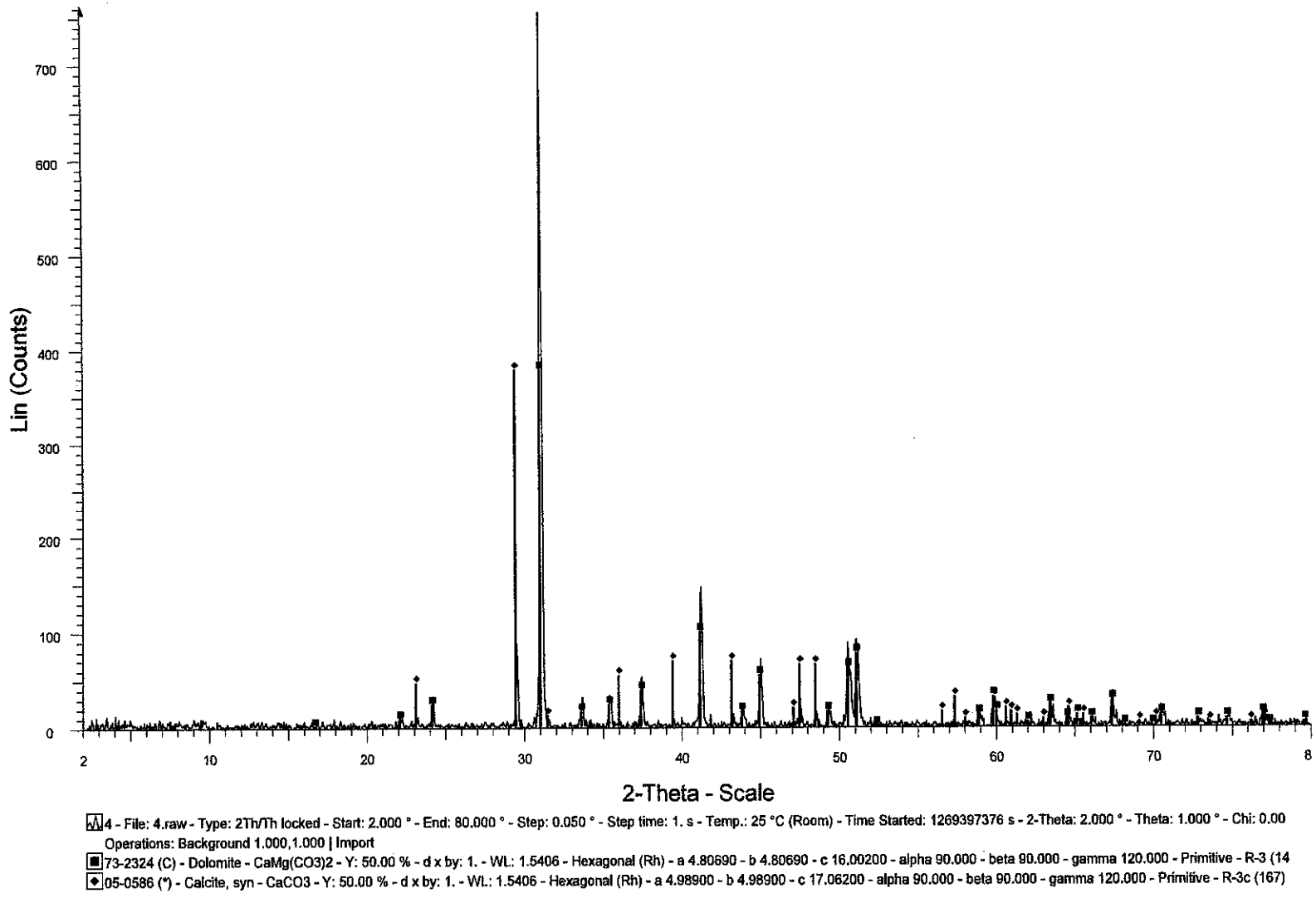

Figure 24 - XRD of dolomite + ethanol at 500°C

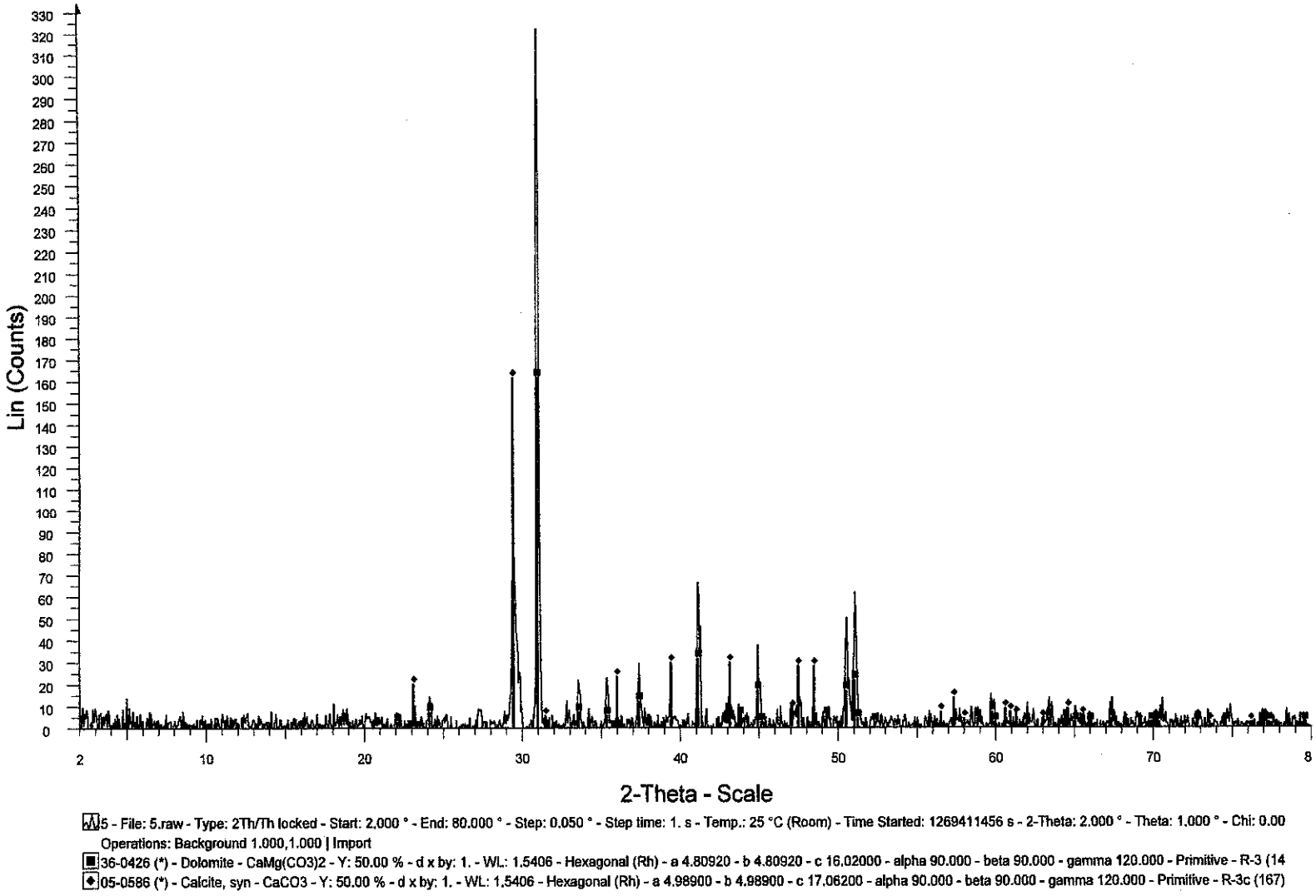

Figure 25 - XRD of dolomite + ethanol at 670°C

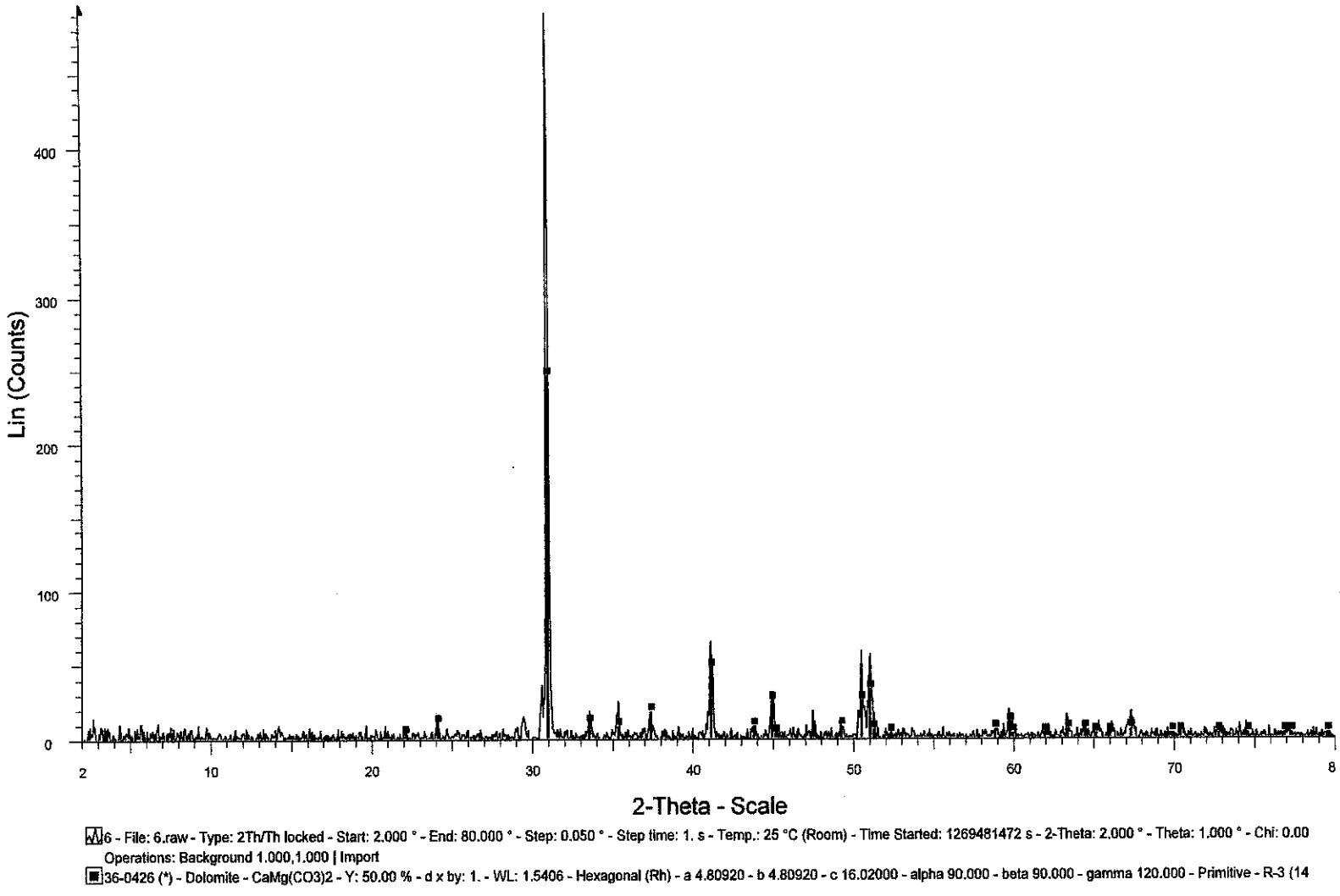

Figure 26 - XRD of dolomite + tert-butanol at 110°C

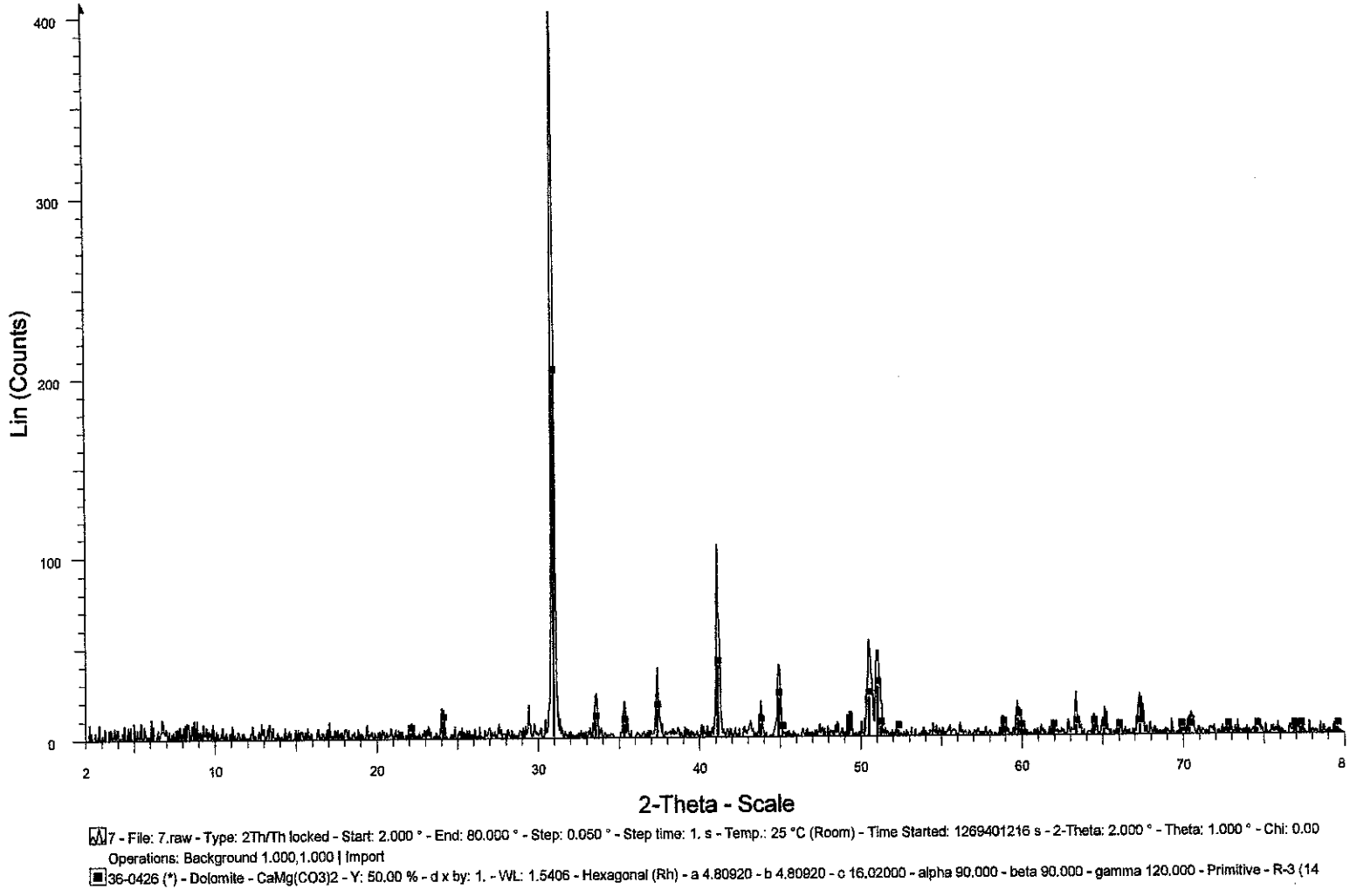

Figure 27 - XRD of dolomite + tert-butanol at 500°C

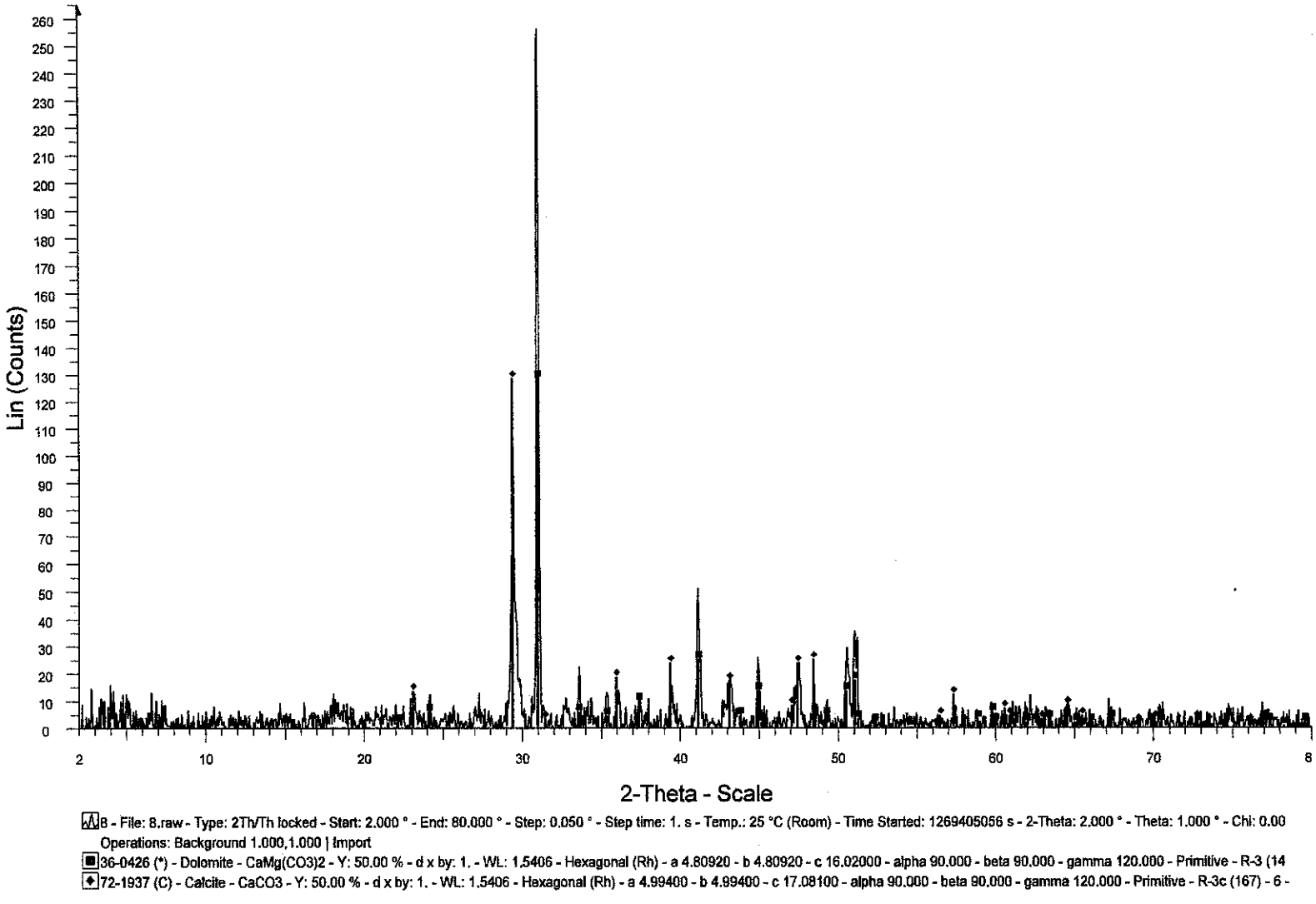

Figure 28 - XRD of dolomite + tert-butanol at 670°C

5.2.1 Basic Principles

X-ray Diffraction (XRD) is a process where the atomic planes of crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. This is the X-ray diffraction phenomenon.

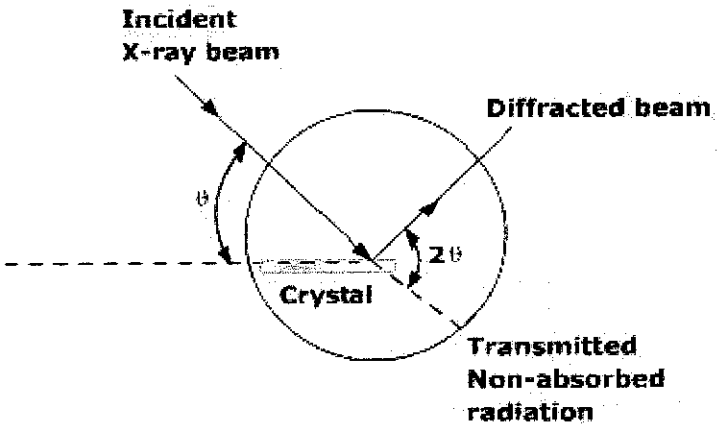

Figure 29 - Basic Principle of XRD

Source: http://image.tutorvista.com/content/solid-state/x-ray-diffraction--representation.jpeg

XRD is based on the Bragg's Law. Where the law is representing with an equation of

$$n\lambda = 2\,d\sin\theta$$

n = an integer
λ = wavelength of the incident X-ray beam

5.2.2 Summary of XRD analysis

From the results obtained from XRD, we can see the similar pattern where the dried temperature, 110°C the peak produced just for crystalline dolomite. Even though there is a small value of peak at this temperature, it still not obvious compared to the maximum temperature of the samples. There are two obvious peaks at the 670°C samples. The peaks produced from the crystalline calcite and crystalline dolomite. The data indicate that there are still significant amounts of un-calcined dolomite still within the particles. This data correlates with the specific surface area data discussed before and is further evidence if an un-reacted core of dolomite. Table below shows the results obtained for three of the samples at three different temperatures.

mples	Dolomite + Water	Dolomite + Ethanol	Dolomite + Tert-Butanol
10°C	- Highest peak is crystalline dolomite at 2θ = 31 - No obvious 2nd peak	- Highest peak is crystalline dolomite at 2θ = 31 - No obvious 2nd peak	- Highest peak is crystalline dolomite at 2θ = 31 - No obvious 2nd peak
90°C	- Highest peak is crystalline dolomite at 2θ = 31 - No obvious 2nd peak	- Highest peak is crystalline dolomite at 2θ = 31 - 2nd peak is crystalline calcite at 2θ = 29	- Highest peak is crystalline dolomite at 2θ = 31 - No obvious 2nd peak
70°C	- Highest peak is calcium carbonate at 2θ = 29 - 2nd peak is crystalline dolomite at 2θ = 31	- Highest peak is crystalline dolomite at 2θ = 31 - 2nd peak is crystalline calcite at 2θ = 29	- Highest peak is crystalline dolomite at 2θ = 31 - 2nd peak is crystalline calcite at 2θ = 29

Table 2 - XRD results

5.3 Surface analysis using BET method

Samples sent to the lab for mesopores analyzing already degassed for 4-5 hours. Unfortunately there are no results obtained from the analysis due to equipment problem. The nitrogen tank is not sufficient enough for the analysis at the moment. The Nitrogen tank need to be refill back and it will take at least one week based on the supplier words.

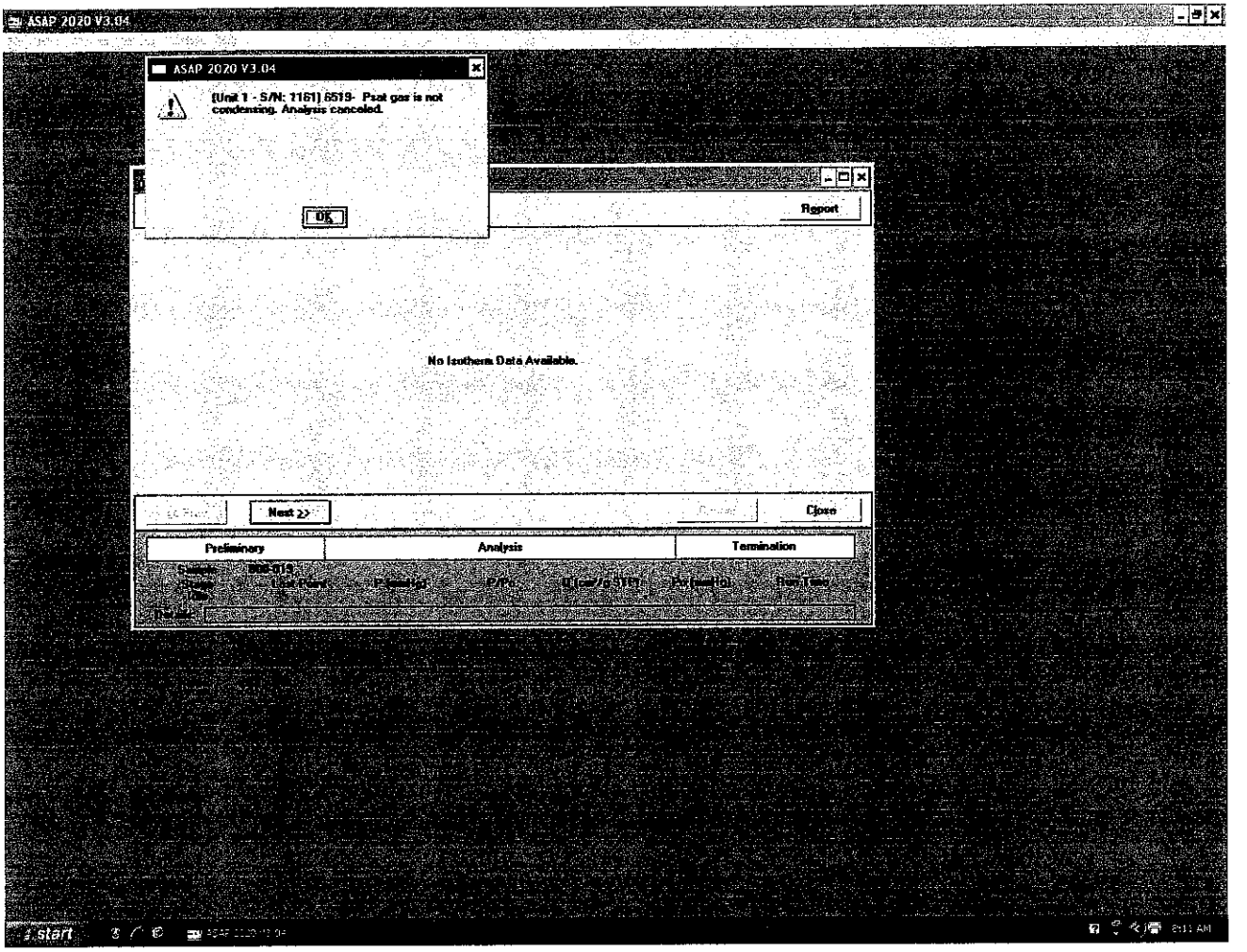

Figure 30 - Error message due to less nitrogen gas

5.4 Carbon Dioxide adsorption using TPDRO

As for this phase, the samples chosen were the one that treated at highest temperature where the calcinations already take place. The current results obtained shown below

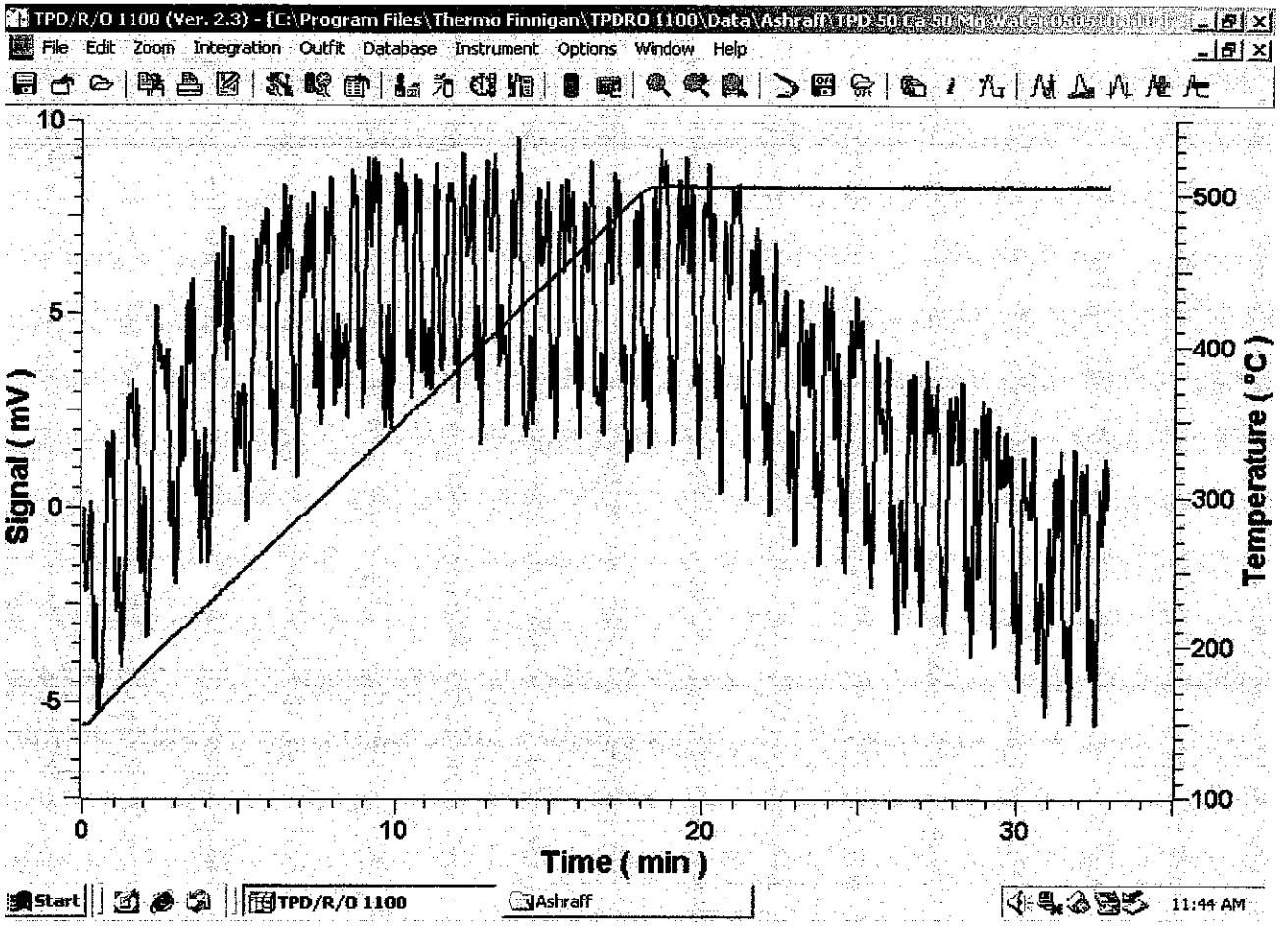

Figure 31 - Graph signal of Carbon Dioxide adsorption using Dolomite + water samples

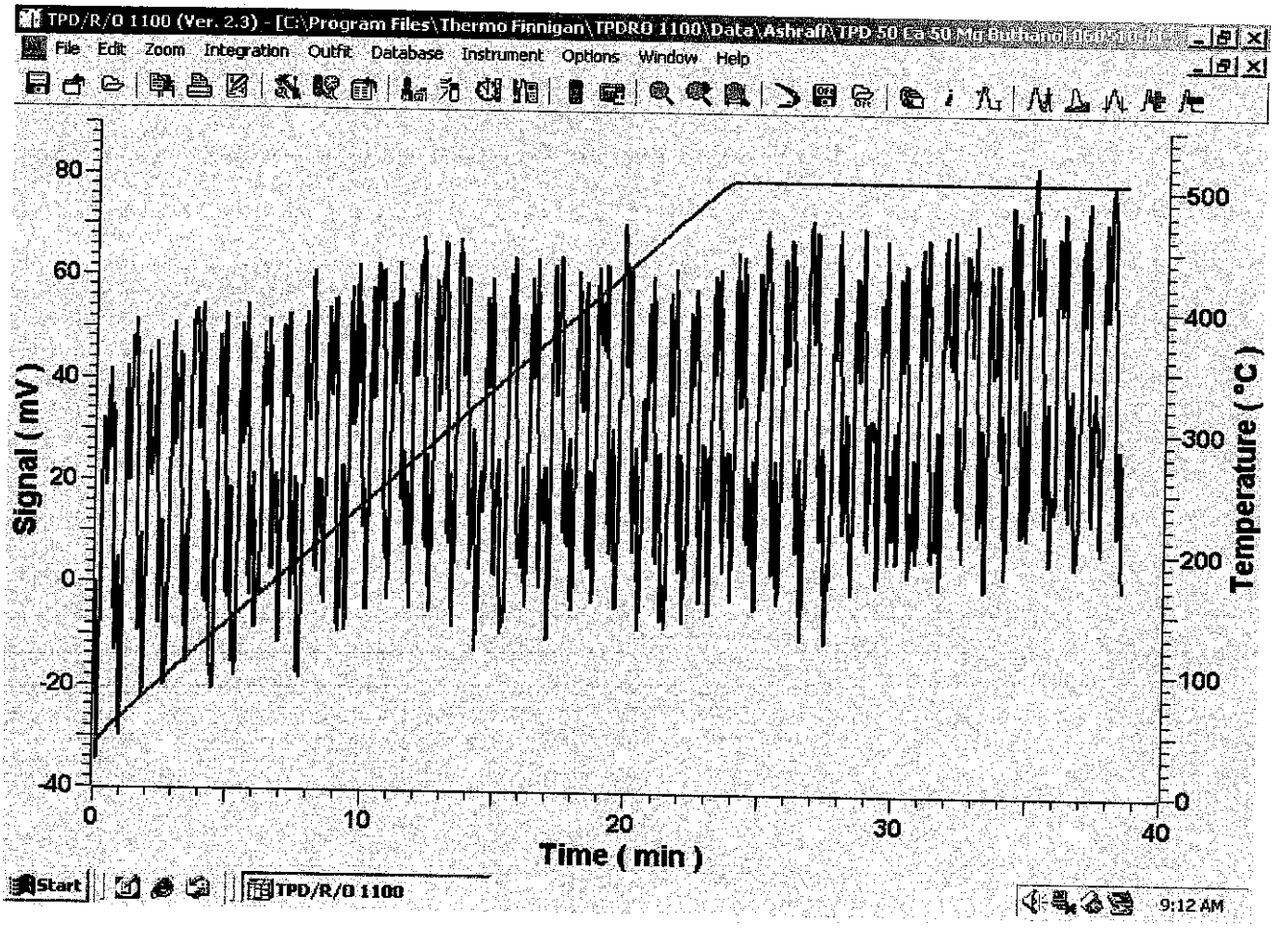

Figure 32 - Graph signal of Carbon Dioxide adsorption using Dolomite + tert-butanol samples

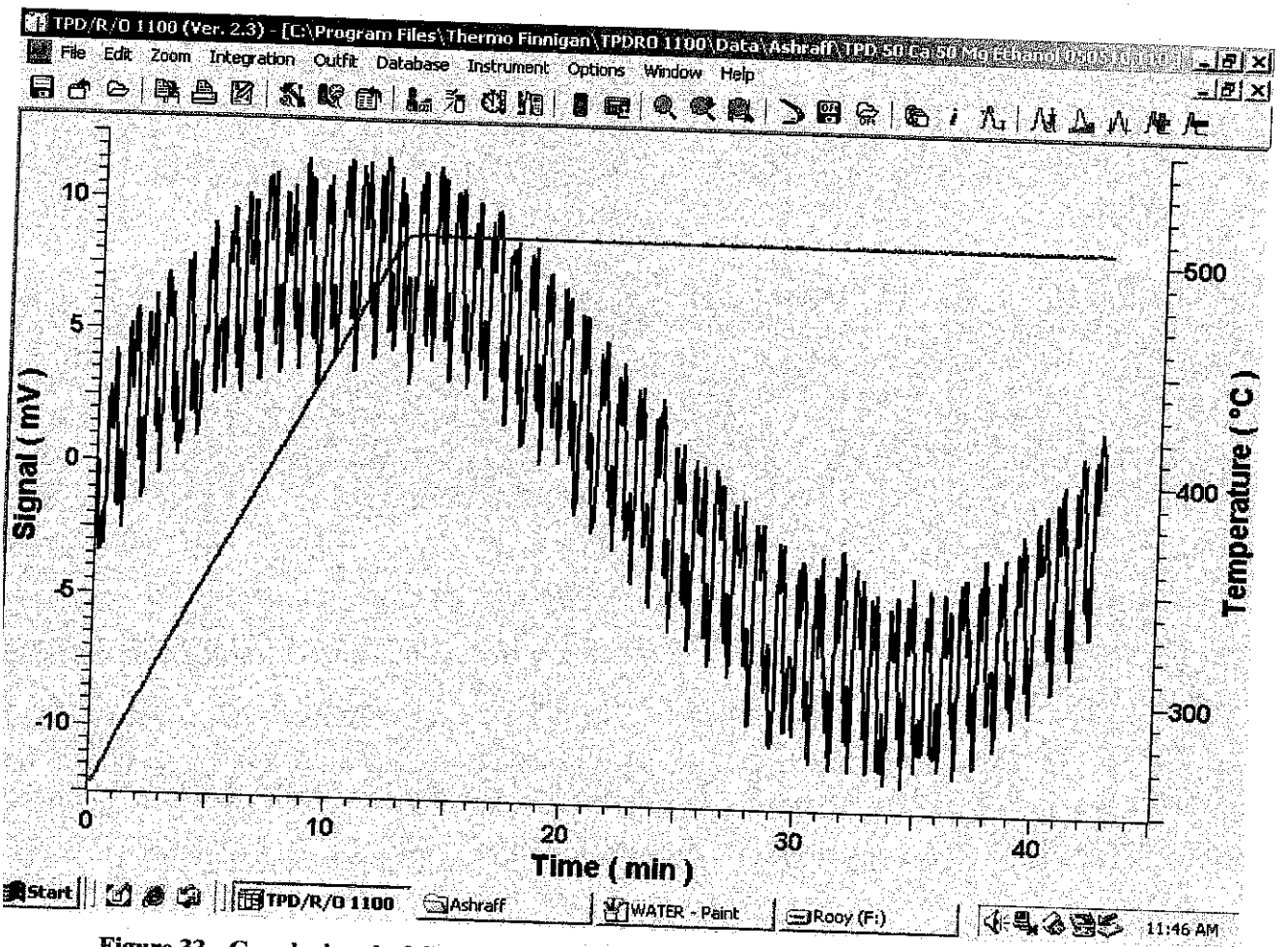

Figure 33 - Graph signal of Carbon Dioxide adsorption using Dolomite + Ethanol samples

TPD/R/O 1100

Thermo Electron

Standard Data Report

Run Nr.:895

File: C:\Program Files\Thermo Finnigan\TPDRO 1100\Data\Ashraff\TPD 50 Ca 50 Mg Water 050510.110
Comment:
Operator: Asnizam
Room Temperature 28°C

Atmospheric Pressure 1000hPa

Sample

Producer: Ashraff
Name: Ca Mg
Mass: 0.2416 g
Info:
Preparation:

Sample-Code: 0
Customer-Code: 0
Support:
Metals: 0

Pretreatment

Name: Pre CO2
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven
Started: 5/5/2010 at 8:40:04 AM finished 9:31:33 AM

Info:

Phase	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp[°C/min]	Stop at T [°C]	Hold for [min]
Cleaning	Nitrogen	20	110°C			5
1:	Carbon Dioxide	20	Off	20	500	15
2:	Off					
3:	Off					
4:	Off					

End Pretreatment with Oven Off

TPD/R/O

Method Name: TPD CO2 Info:
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven
Started: 5/5/2010 at 10:21:03 AM finished 10:54:08 AM
Gas Port when Ready: (b) Helium
Gas Port when End:
Sample rate: 1 s
Gain: 10
Polarity: Negative

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp°C/min	Stop at T [°C]	Hold for [min]
Helium	20	Off	20	500	15

Results

Amount gas adsorbed: 0.00000 µmol/g

Baseline

Start at 0.0167 min -257.56836 mV. Stop at 32.9167 min -312.19482 mV

Calibration

Use Calibration Factor: 0.000000 *10e-7 mmol/mVs

Peaks

#	Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[µmol/g]	[%]
1	0.0000	0.0000	0.0000	0	0.00	0.00000	0.00

Standard Data Report

Run Nr.:900

File: C:\Program Files\Thermo Finnigan\TPDRO 1100\Data\Ashraff\TPD 50 Ca 50 Mg Buthanol 060510.110
Comment:
Operator: Roy
Room Temperature 30°C

Atmospheric Pressure 1000hPa

Sample

Producer: Ashraff
Name: Ca Mg
Mass: 0.3069 g
Info:
Preparation:

Sample-Code: 0
Customer-Code: 0
Support:
Metals: 0

Pretreatment

Name: Pre CO2
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven
Started: 5/6/2010 at 12:07:58 PM finished 12:58:26 PM

Info:

Phase	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp[°C/min]	Stop at T [°C]	Hold for [min]
Cleaning	Nitrogen	20	Off			5
1:	Carbon Dioxide	20	Off	20	500	15
2:	Off					
3:	Off					
4:	Off					

End Pretreatment with Oven Off

TPD/R/O

Method Name: TPD CO2

Info:

On Instrument: TPDRO 1100 with Ser.Nr.2005305 / on Left Oven
Started: 5/6/2010 at 3:24:45 PM finished 4:03:27 PM
Gas Port when Ready: (b) Helium
Gas Port when End: (b) Helium
Sample rate: 1 s
Gain: 1
Polarity: Positive

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp°C/min	Stop at T [°C]	Hold for [min]
Helium	20	Off	20	500	15

Results

Amount gas adsorbed: 0.00000 µmol/g

Baseline

Start at 0.0167 min 197.34701 mV. Stop at 38.5167 min 76.80257 mV

Calibration

Use Calibration Factor: 0.000000 *10e-7 mmol/mVs

Peaks

#	Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[µmol/g]	[%]
1	0.0000	0.0000	0.0000	0	0.00	0.00000	0.00

TPD/R/O 1100

Thermo Electron

Standard Data Report

Run Nr.:896

File: C:\Program Files\Thermo Finnigan\TPDRO 1100\Data\Ashraff\TPD 50 Ca 50 Mg Ethanol 050510.110
Comment:
Operator: Asnizam
Room Temperature 28°C

Atmospheric Pressure 1000hPa

Sample

Producer: Ashraff
Name: Ca Mg
Mass: 0.3085 g
Info:
Preparation:

Sample-Code: 0
Customer-Code: 0
Support:
Metals: 0

Pretreatment

Name: Pre CO2
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven
Started: 5/5/2010 at 3:31:51 PM finished 3:31:53 PM

Info:

Phase	With Gas	Flow [ccm/min]	Start at T [°C]	Ramp[°C/min]	Stop at T [°C]	Hold for [min]
Cleaning	Nitrogen	20	110°C			5
1:	Carbon Dioxide	20	Off	20	500	60
2:	Off					
3:	Off					
4:	Off					

End Pretreatment with Oven Off

TPD/R/O

Method Name: TPD CO2 Info:
On Instrument: TPDRO 1100 with Ser.Nr.20033057 on Left Oven
Started: 5/5/2010 at 5:23:19 PM finished 6:06:17 PM
Gas Port when Ready: (b) Helium
Gas Port when End:
Sample rate: 1 s
Gain: 10
Polarity: Negative

With Gas	Flow [ccm/min]	Start at T [°C]	Ramp°C/min	Stop at T [°C]	Hold for [min]
Helium	20	Off	20	500	30

Results

Amount gas adsorbed: 0.00000 µmol/g

Baseline

Start at 0.0167 min -353.39356 mV. Stop at 42.8167 min -428.26335 mV

Calibration

Use Calibration Factor: 0.000000 *10e-7 mmol/mVs

Peaks

#	Start [min]	Stop [min]	Maximum [min]	T [°C]	Integral [mVs]	[µmol/g]	[%]
1	0.0000	0.0000	0.0000	0	0.00	0.00000	0.00

From the result obtained for dolomite+water sample, can see that there is no adsorption amount stated. This is because there is no gas successfully adsorbed by the samples. For the second run using dolomite+tert-butanol sample, the final result is still the same with the previous sample. As a modification, the third run using dolomite+ethanol samples the holding time phase is being held longer than before. But still after at the end of the process, there is still no amount of gas adsorbed detected.

Regarding this, there are some discussion being made after a few discussions with the technician and my supervisor. Theoretically, the calcine dolomite should be a good absorber but in this case from the final result, there is none amount stated by the instrument.

The possibilities of this unwanted result are:

1. The method being used during the process is not a preferable method. Supposedly, this process needs a mixture of CO_2/N_2 gas tank in order to obtain some signal from the graph. Instead of that, we are using pure N_2 and pure CO_2 during the pre-treatment, and using Helium gas during TPD phase. This try and error method does not give any result which can be concluded as not a good way to study the adsorption of CO_2 on dolomite.
2. The samples are held at a short duration. The samples might need a longer time for the adsorption process.

CHAPTER 6
CONCLUSION

From the current results obtained, the objective of my project to study the effectiveness arbon dioxide adsorption using solvothermolyzed dolomite is not giving the desired results. A ew discussions with my supervisor came with conclusions which are

1. The adsorption method used in this project which is using the TPDRO is not a prefer method. By supplying two pure acidic gases from different tanks will give no signal of adsorption using TPDRO. It is better to use the mixture gases tank to see a better result.
2. The time for CO_2 pre-treatment is not long enough during holding phase in order to let the samples to adsorb the gas.
3. The samples are not calcined at the desired temperature which is 900°C. This is due to the old furnace used that cannot reach the desired temperature.

So, as a final conclusion, this project is not achieved its target to study the effectiveness arbon dioxide adsorption using solvothermolyzed dolomite due to some instruments problem. he research should be further studied because from the analysis shown that the surface area of he dolomite was significantly increased by thermal treatment which resulted in sorbent roperties that are particularly suited to the adsorption of gaseous pollutants. Generally the apacity for gaseous adsorption increased with the greater char time and char temperature. So, by heoretically dolomite is a good adsorber and it has a potential to act as adsorbents for acidic ases, albeit with a relatively low surface area compared to commercial adsorbents.

References

1. A. Duffy, G.M. Walker *, S.J. Allen, Investigations on the adsorption of acidic gases using activated dolomite (2006) pp. 239-244

2. KristoÂf-MakoÂ*, A.Z. JuhaÂsz, The effect of mechanical treatment on the crystal structure and thermal decomposition of dolomite (1999) pp. 105-114

3. P.G. Caceres and E. K. Attiogbe, Thermal Decomposition of Dolomite and the Extraction of Its Constituents (1997) pp. 1165-1175

4. Bernard Castagne´de *, Alexei Moussatov, Denis Lafarge, Mohamed Saeid, Low frequency in situ metrology of absorption and dispersion of sound absorbing porous materials based on high power ultrasonic non-linearly demodulated waves (2008) pp. 634-648

5. Ying-jie Li, Chang-sui Zhao□, Lun-bo Duan, Cai Liang, Qing-zhao Li, Wu Zhou, Hui-chao Chen, Cyclic calcination/carbonation looping of dolomite modified with acetic acid for CO2 capture (2008) 1461–1469

6. W. H. Macintire,T. B. Stanseli ,Steam Catalvsis in Calcinations of J Dolomite and Limestone Fines pp. 1548

7. Leslie A. Sherman and Phillip Barak, Solubility and Dissolution Kinetics of Dolomite in Ca–Mg–HCO3/CO3 Solution at 258C and 0.1 MPa Carbon Dioxide (2000) pp. 1959-1968

8. Philip Engler, Mark W. Santana, Martin L. Mittleman, David Balazs, Non-Isothermal in Situ XRD Analysis of Dolomite Decomposition (1988) pp. 3-8

9. J. Nishino, Adsorption of water vapor and carbon dioxide at carboxylic functional groups in the surface of coal (2000) pp. 757-764

10. Kenzi Suzuki, Aichi-ken, Keiichi Inukai Method for Selective Separation of Carbon Dioxide from Waste Gas of Combustion (1996)

11. TPDRO Product Manual from www.thermo.com

12. Scott McFarlane, U.S. Geological Survey Central Region Research Projects http://wwwbrr.cr.usgs.gov/projects/GW_Unsat/vs2di/hlp/solute/freundlich.html

13. G. Tyler Miller , Living in the Environment, http://www.lenntech.com/carbon-dioxide.htm

14. TPDRO 1110, Copyright 2007 Affiniti Analytical http://affiniti-analytical.com/TPDRO.html

15. Tom Socha, Air Pollution Causes and Effects
http://healthandenergy.com/air_pollution_causes.htm
16. N.S.Imyanitov, Unimolecular Nucleophilic Substitution does not Exist!
http://sciteclibrary.ru/eng/catalog/pages/9330.html
17. Compiled by A. D. McNaught and A. Wilkinson, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")
http://goldbook.iupac.org/S05762.html
18. Wastewater Engineering; Metcalf & Eddy; third edition; 1991; page 317
http://www.lenntech.com/library/adsorption/adsorption.htm
19. David Barthelmy, Mineralogy Database
http://webmineral.com/data/Dolomite.shtml